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Methodology for Collecting and Analyzing Organic Air Pollutants

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February 1979

METHODOLOGY FOR COLLECTING AND ANALYZING ORGANIC AIR POLLUTANTS

by

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A number of support-bonded liquid phase sorption media were developed and evaluated in model systems for collecting and analyzing organic air pollutants. Polymers with various functional groups were synthesized and chemically bonded onto inert supports in thick layers. A media consisting of a silicone liquid bonded to Chromosorb W was used with excellent results. Retention times of most organic compounds on this liquid are extremely long at ambient temperatures, and sampling can be carried out for 24 hours at a rate of 10 liters of air per minute. In contrast, subsequent counter current liquid extraction takes only a few minutes since retention volumes are very small. Extracts were analyzed largely by gas chromatography.

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SECTION 1

INTRODUCTION

One usually thinks of air pollution in terms of its most obnoxious constituents: Sulfur dioxide, peroxyacetylnitrate, particulate matter, and so forth. The area of organic compounds of higher molecular weight has, in comparison, been much less investigated. Of course, we are familiar with the role of hydrocarbons from automobile exhausts in the production of smog, with the occasional severe agricultural damage done by pesticides translocated by wind, and with the presence of potent carcinogens originating from combustion processes.

The last few years have seen a tremendous increase in our knowledge on the constitutents of air, not only because of increased public interest, but also because of suitable, highly sensitive instrumentation which has become available recently. Two examples in point may be the use of capillary columns in gas chromatography, and the use of computer-interfaced high-resolution mass spectrometers connected via molecular separator to a gas chromatograph. Although many compounds have been identified, it is safe to assume that a myriad more exists in air at trace levels--beneficial, neutral, or detrimental to man.

Historically, the collection of air-borne organics (in gaseous, not particulate form) has often been a much harder task than their subsequent analysis. Collection is generally performed by

a. condensation in cold traps, usually at the temperature of liquid nitrogen or dry ice,

b. bubbling or impinging air on such compounds as ethyleneglycol or hexyleneglycol which are subsequently extracted wtih an organic solvent,

c. trapping on solid absorbents such as activated carbon, or

d. sorption on typical gas chromatographic phases of the liquid-coated supported or the resin particle type.

These methods suffer from certain drawbacks. Labile compounds can decompose or rearrange on the highly catalytic carbon surface. The atmosphere contains considerable amounts of water and sometimes the oxides of sulfur and nitrogen in substantial quantities--all of which condense at liquid nitrogen temperatures. Furthermore, the cryogenic methods need suitable technical equipment and are difficult to operate under field conditions. GLC-type phases must be heated to re-vaporize the collected materials and generally permit only one chromatographic run. The literature describing the techniques for, and the difficulties associated with, the collection of airborne organics is quite extensive.

This report describes the development of solid media for the collection of organic pollutants in air. It includes the work accomplished between the submission of the proposal and the final award of the EPA grant R-801050. In the following pages, highlights of typical achievements will be presented briefly. For a complete list of achievements, please refer to the list of publications supported by this grant.

SECTION 2

CONCLUSIONS

The ideal method for collecting organic air pollutants would be one which is not affected by water and acidic inorganic compounds in the atmosphere, which can be easily used at remote locations, minimizes decomposition of the collected substances, and collects organics in a form suitable for various types of subsequent analyses. The collection of all organic air pollutants--except those of very high volatility--with support-bonded liquid phases represents a superior method compared to other techniques of collection.

A highly loaded, support-bonded silicone liquid phase--ca. 30% to 40% ($C_{18}H_{37}O_{3/2}$) on Chromosorb-W 30/60--was used with excellent results for the collection of organics from air under various circumstances. Retention times of most organic compounds on this phase are extremely long at ambient temperature, and sampling can be carried out for 24 hours at a rate of 10 liters per minute--with only the most volatile compounds breaking through at the exit of the small cartridge containing the support-bonded polymer. In contrast to these long retention times, retention volumes in liquid extraction are extremely small and the countercurrent extraction of a cartridge is completed in a few minutes.

For the purpose of liquid extraction, a prototype apparatus which allows the continuous recycling of low-boiling solvent was constructed. This approach had become feasible only through the fact that the 40-odd percent of silicone and other polymers are completely support-bonded and none of it is extractable, no matter what solvent (including alcohols, water or acids) is used. The low boiling point of the extracting solvents--preferentially pentane or dichloromethane--allows easy concentration of the extracts, averts evaporation losses and minimizes decomposition of heat-labile compounds. Pentane is an ideal solvent for later use with the alkali flame or electron capture detectors, dichloromethane is very well suited for the flame ionization detector.

The organic compounds enrich in solid collection media could be released not only by liquid extraction but also by heat desorption. The later is preferred when the collecting media is critically tested for inertness and/or catalytic decomposition. Details of the collection and desorption ports and the various simultaneous flow patterns of the system are shown in the report. Initially, chromatograms for the different modes of sample introduction--direct injection to GC, direct injection through the hot cartridge, and heat desorption of cartridge loaded with test mixture from doped air--is compared to establish the performance of the system. The well-known technique of venting (solvent or solute) can serve to introduce only desired retention ranges from

a loaded cartridge into the gas chromatograph; loop injection is facilitated by the two valve system. In actual field sampling, the collection assembly has the ease of portable handling and the "loaded" cartridge can easily be transported to the laboratory.

Support-bonded liquid phases were extended from the polysiloxanes to other polar and non-polar polymers, i.e. Carbowax 20M, AN-600, ON 870, FFAP, OV101, SE-30 and linear polyethylene. Further, the solid support bonded to the organic moiety was extended to the naturally occuring diatomaceous earths to the man-made silica gels. The latter materials were modified by treating with water under high pressure followed by bonding with organic polymers.

A wide series of different surface areas, large pore, adsorbents have been prepared from available silica gel. The materials were deactivated to produce semi-selective phases. The report described the technique used to vary the surface area of the gel and the deposition of organic surface modifiers. The potential use of the otherwise too retentive silica gel as support for chromatography is characterized by the GC performance of polar and non-polar compounds. The retention volumes of polar solutes (which are irreversibly adsorbed on the authentic silica gel) are correlated to the size of the pores, i.e., surface areas, on one hand, and/or the properties of the surface modifier on the other. Non-polar solutes though affected less significantly, generally become early eluters as the accessible areas decrease and in the absence of deactivators. Applications of the adsorbents as solid media to collect organic pollutants in air as well as industrial organic vapors in working atmospheres have been investigated under a wide range of conditions. The cutoff of trapping efficiency or the breakthrough, of the vapors, are studied as functions of such parameters as volatility and structure of the compounds, flow rate of sampling and humidity of the atmosphere.

The most promising collection media were used for sampling of (a) standards, including chlorinated hydrocarbon insecticides, (b) automobile exhaust, and (c) the relatively clean air of the University of Missouri campus at Columbia. Standards were quantitatively recovered; virtually no heavier organic compounds came through the cartridge in spite of hugh amounts of water and a heavy load of hydrocarbons emitted from the exhaust pipe; and finally, even the clean campus air was shown to contain a multitude of peaks. These results certainly indicate the broad potential of our appproach to the analysis of air pollutants.

SECTION 3

RECOMMENDATION

Based on the work done under this grant, we can make the following recommendations:

SOLID COLLECTION MEDIA

Solid collection media are recommended for the collection of volatile organics in air. These media are far superior to the liquid media used in impinger type samplers. They offer better collection efficiency, greater ease of handling, more flexibility in manupilation of analysis, and longer life.

SUPPORT BONDED PHASES

The use of solid collection media with bonded liquid phases are recommended over simpler media such as charcoal and untreated silica gel. Solid support-bonded phases are superior to solid media without a liquid phase because they minimize decomposition of the pollutants of interest, increase the collection efficiency and capacity of the media and provide less sensitivity to changes in humidity and collection flow rates.

LIQUID EXTRACTION

Continuous liquid extraction is recommended for removal of the sample from the collection media when sample decomposition is a serious concern and when analysis by more than one technique is required. A continuous extracting apparatus which is designed to the fit the collection cartridge allows each concentration of the extracts, averts evaporation losses and minimizes decomposition of heat-labile compounds.

HEAT DESORPTION

Heat desorption is recommended for fast routine testing where only a single GC analysis is needed, where the variable parameters are known and where sample decomposition is not a serious concern. For this type of analysis, heat desorption is more cost-effective than liquid extraction. Additional studies of thermal desorption units are recommended in order to minimize sample decomposition. Such sample decomposition may be caused by contact with metals or insulating materials in the desorption unit.

SECTION 4

EXPERIMENTAL PROCEDURES

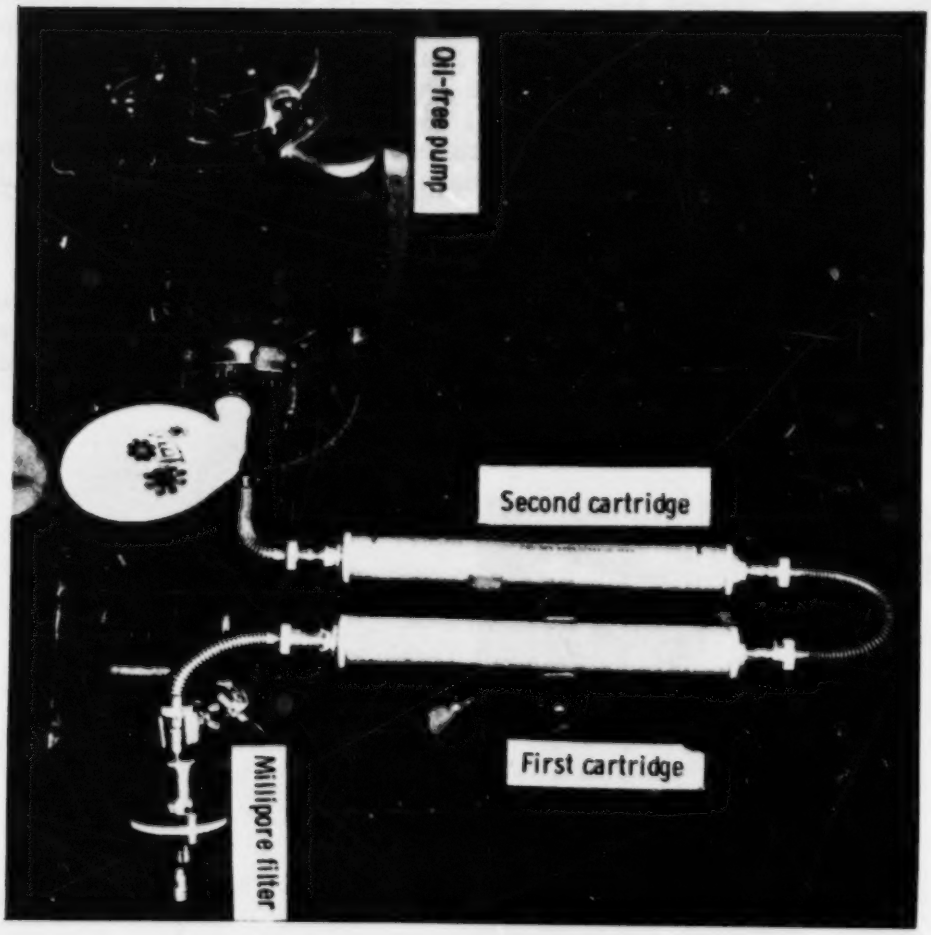
CONSTRUCTION OF A PROTOTYPE AIR SAMPLER

The efficiency of collection depends on several factors. If a certain volume of air is passed through a cylindrical cartridge packed with solid media whose surface is modified with organic liquid layers, the amount of air contaminant collected depends on the partition ratio of the compound at the prevailing temperature as well as the dimensions of the cartridge and its pressure drop from inlet to outlet. Given a certain cartridge volume, a longer cartridge will retain more. However, if a steep pressure differential is necessary to maintain the desired flow, some of the advantages of the longer cartridge may be lost.

In an earlier study (1), the enrichment of organic air contaminants was done by sampling with a single cartridge. To determine which compounds are partially, and which are completely retained under defined sampling conditions, a second cartridge can be inserted between the first cartridge and the pump.

A portion of the present study pursued almost exclusively the two-cartridge approach, mainly because comparison of compounds collected by the first and second cartridges can give important information on collection efficiency and characteristics. The two phases may or may not be the same, depending on the experiment.

Therefore, a two-cartridge sampling apparatus providing 30 l/min air flow rates and featuring easy cartridge changes was constructed. This is shown on Fig. 1. The double-cartridge sampling approach was used throughout the experiments to indicate the breakthrough range (which occurred, in most cases, around Kovats index 1000, i.e., n-decane). Oil-free pumps were connected with Cajon fittings and flexible stainless-steel tubing to two cartridges containing the supported-bonded phases, held in place by stainless-steel screens and glass wool. The flow rate was estimated by measuring the diameter of inflated balloons attached to the pump for a measured time. Air entered the system through a teflon Millipore filter of 5-μ pore size, which was supported by a stainless-steel screen in a modified Millipore filter holder. The cartridges were Chemical Research Service "Hydrocarbon traps." Teflon is the preferred material for the packing rings; if silicone rubber is used, it should be covered by teflon tape to avoid extraneous GLC peaks. The O-rings in the fittings are somewhat less prone to cause trouble. All Cajon Fittings and Flexible tubing were ½ in. nominal, making for facile set-up, take-down or interchange, of the system components.



Typical set-up for atmospheric sampling. The deflated balloon shown is used to roughly estimate the air flow rate for each sampling experiment.

Figure 1

EXTRACTION APPARATUS FOR THE LOADED CARTRIDGE

Fig. 2 shows the set-up used for extraction of collected organics from the traps. The three-necked flask had Clearfit joints, precluding the need for grease. A high-vacuum jacket surrounded the distillation column to avoid excessive reflux. Teflon tubing and adapter ferrules (Scientific Research Service) were used for connections via Swagelok fittings with ½ in. tube extensions. Since these extensions match the Cajon fittings on the cartridge, the latter could be inserted or removed without the use of tools in less than a minute. A brisk flow of solvent pentane or other liquids of high purity and volatility--was maintained for approximately 15 min after the cartridge overflowed into the flask.

The pentane extract was concentrated, first in a flask and then in a graduated tube, to ca. 0.3 ml or less by blowing dry, pure nitrogen at the surface of the liquid. If further concentration was required, the extract was transferred to a capillary tube and concentrated with nitrogen introduced through a syringe needle.

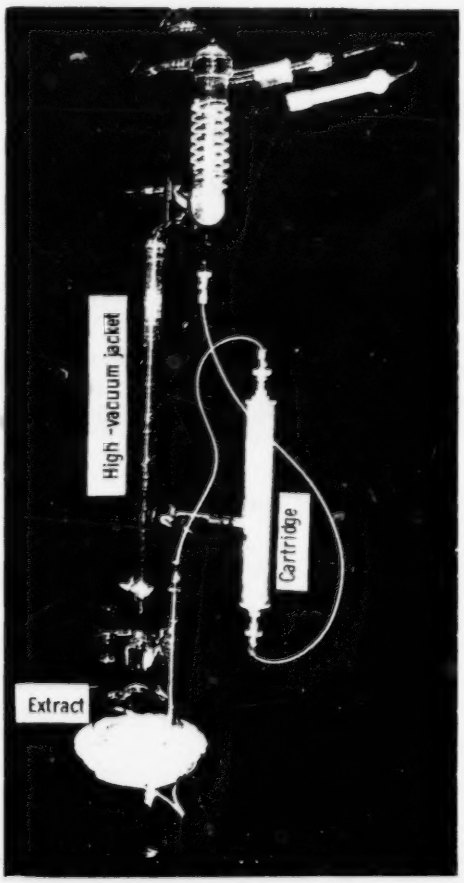


Figure 2

Set-up for extraction of collected air contaminants. Freshly distilled solvent enters the cartridge at the bottom and overflows back into the flask.

SILICONES BONDED TO DIATOMACEOUS EARTHS AS COLLECTION MEDIA

Support-bonded silicones possess three characteristics for collecting, and thus concentrating, small amounts of organics from the atmosphere or natural water systems: They are inert and hydrophobic, they can be produced in very thick layers and various compositions and, most importantly, they are non-extractable by any conceivable solvent short of sulfuric acid. Thus, the atmosphere or water can be passed through a bed of a suitable silicone phase, and the phase later extracted with an organic solvent to release the collected organics. This approach has been shown to allow fairly easy analysis of difficult-to-analyze gaseous air pollutants in the parts per billion range, and certain water pollutants (chlorinated hydrocarbon insecticides, PCB's, etc.) in the parts per trillion range. These studies were highly successful.

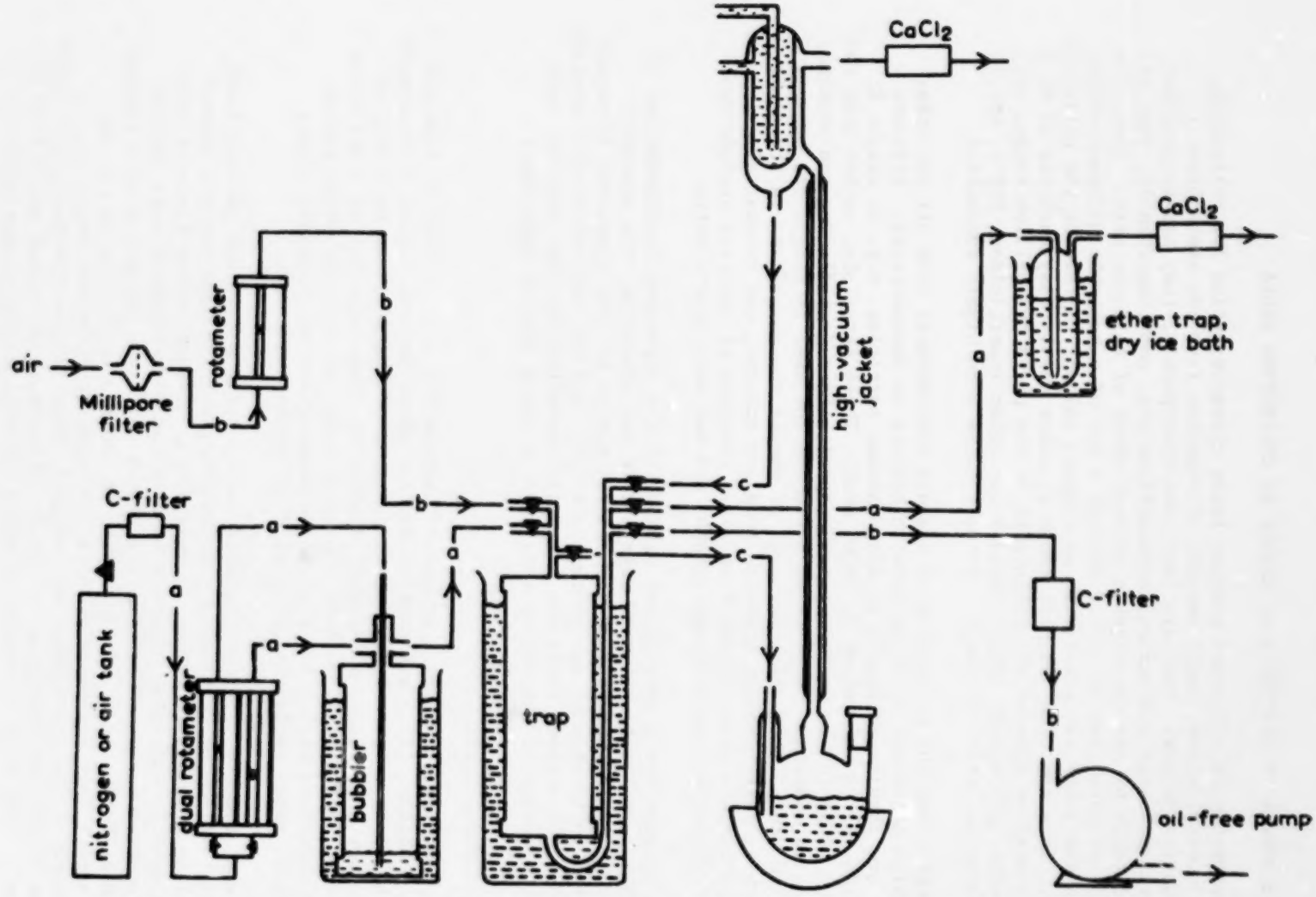
A method for the collection of organic contaminants from air and other gases, which makes use of these novel materials is demonstrated. Silicone polymers are chemically bonded to diatomaceous particles, e.g. 26 weight % $(C_{18}H_{37}SiO_{3/2})_n$ to Chromosorb W, 30/60 mesh. These materials, packed into two cartridges connected in series, remove organics from fast-flowing gas streams. The collected compounds can then be extracted and used to analytical or preparative ends. This phase was used to sample the atmosphere in St. Louis and Columbia, collection of organics from car exhaust, and removal of chlorinated hydrocarbon insecticides from air. Examples of analysis include dual-channel EC/FID gas-liquid chromatography and GLC mass spectrometry.

Fig. 3 provides a generalized picture of the apparatus configurations of the initial experiments. Lumped together in one prototype, the schematic shows how the cartridge is used for the collection of test compounds (flowpath a), for the collection of air contaminants (b), and for extraction with pentane (c). Since the various parts can be easily connected and disconnected, only pertinent elements of the set-up were used in the following experiments.

Cartridges and Phases

A commercial, charcoal-containing "hydrocarbon trap" (Chemical Research Services, Addison, Ill.) was emptied and the aluminum hull filled with support-bonded phases held by stainless-steel screens. The end-pieces were drilled out to accept ½ in. Cajon fittings. Similar fittings were put on a Millipore filter holder and an oilless Bell & Gossett pump, so that the whole system could be connected with ½ in. o.d. Cajon stainless-steel flexible tubing. (This tubing rusts profusely and should be treated with care.)

Several types of supports, coated with polymer of various percent loads, were used to fill the cartridges. Octadecyltrichlorosilane was the monomer for all liquid phases mentioned in this paper, however, other types of polymers are equally suitalbe. Support bonding and polmerization were carried out as reported earlier (2). The raw phases were then extracted with benzene in a soxhlet for at least 30 hours with as short a cycle time as was considered safe. This procedure removes any non-support-bonded material. A small amount of the dried phase was weighed, kept in a muffle furnace at 1000° for three hours, and reweighed to obtain an estimate of liquid phase load (= "ignition"). The bulk of the dried phase was filled into a cartridge and



Initial laboratory set-up for collecting organics on, and extracting them from, support-bonded silicone phases contained in the "trap". a, Test compound sampling; b, atmosphere sampling; c, extraction.

Figure 3

extracted with pentane in a set-up according to Fig. 3 (c), then produced the first blank before actual use for sampling.

The various phases serving in this investigation had the following minimum liquid loads as determined by ignition: 14 and 16% on Chromosorb G 45/60, 24% on Chromosorb A 20/30, 28 and 31% on Diatom W 20/40, and 26% on Chromosorb W 30/60 mesh. A typical experiment is described below.

Collection

Atmosphere Samples--

The schematic presented in Fig. 3(b) was carried out in field sampling as follows: The Millipore filter holder was connected with flexible SS tubing to the first cartridge, the first to the second cartridge, and the second cartridge directly to the pump. The approximate air flow through the system was measured by attaching deflated balloons to the pump exhaust and calculating the air flow after a certain time interval from the diameter of the inflated balloon. Sampling was carried out in the downtown section of Columbia, and downtown and industrial sections of St. Louis.

Car Exhaust Samples--

A similar arrangement was used to sample car exhaust, the filter holder being connected fo a funnel held, upside down, just above the end of the exhaust pipe. The warmed-up V-8 was idling during the experiment.

Other Test Samples--

Using the bubbler shown in Fig. 3(a), two types of mixtures were sampled. First, a small amount of gasoline--the same as used in the car exhaust experiment--and second, a mixture of common chlorinated hydrocarbon insecticides. In the latter case, a slow stream of nitrogen swept through the heated bubbler and carried the substances into a much larger stream of laboratory air. This air was drawn in through an activated carbon filter, doped with sample in the bubbler as described, and flowed then through the Millipore teflon filter, the two cartridges, a dry ice trap, and finally, the pump. The use of air rather than nitrogen was chosen to combine better simulation of atmospheric sampling with reduced expenditures.

Thermostating of the trap, as shown in Fig. 3, was used only in preliminary tests; all experiments mentioned were run at ambient temperatures.

Extraction

The schematic shown in Fig. 3(c) was followed. The three-necked flask with Clearfit joints (no grease) was charged with at least 200 ml "chromatographically pure" pentane and brought to a rapid boil. When the cartridge had filled up and began discharging pentane back into the flask, a brisk flow was maintained for ca. 15 minutes. The solution from the flask (excluding the solvent left in the cartridge) was concentrated to 0.3 ml in a tube suspended in water of ambient temperature, by blowing dry nitrogen at the surface of the solution.

The extraction was performed in a countercurrent manner, i.e. the flow of gas during sampling and the flow of liquid during extraction occurred in reverse directions. Teflon tubing was used to connect the cartridge with the reflux condenser and the fask via ½ o.d., 1/8 i.d. adapters, which fitted into the Cajon terminals of the cartridge. Assembly and disassembly of this set-up can thus be achieved in a few seconds and cartridges can be extracted at a rapid rate.

Analysis by GLC

Several types of analysis based on gas-liquid chromatography were performed, and they are described below in random succession.

All samples were first analyzed on a 20 foot, 2.5 mm i.d. glass column filled with 3% OV-101 on Chromosorb W, H.P., 80/100 mesh, in a Microtec MT-220 gas chromatograph equipped with a hydrogen flame detector. Samples and blanks were usually followed by a mixture of n-hydrocarbons to allow a rough estimate of Kovats indices under the particular temperature program chosen.

No such program was possible, of course, with the Ni-63 electron capture detector. This detector was used in two configurations--alone, and in a micro-capillary valve (Precision Sampling, Baton Route, La.) inside the column oven to regulate the split ratio.

The pesticide samples were run on the EC detector only, the car exhaust samples were analyzed with the splitting arrangement. Read on a dual-channel recorder, the two detectors can yield some information about the polarity of the eluting compounds.

An air sample from the Columbia campus, which contained a greater number of FID peaks, was also run with an alkali flame and a flame photometric detector, but failed to exhibit peaks indicative of phosphorus-containing compounds. The sulfur channel of the flame photometric detector was used in a temperature-programmed analysis to show the presence of a few sulfur-containing compounds in gasoline and car exhaust.

A car exhaust sample was further used to demonstrate its analysis by a combined gas chromatograph-mass spectrometer (Packard-CEC 110B) system with a Watson-Biemann separator and direct oscillographic recording.

Results and Discussion

All results lumped together, support-bonded silicone phases behaved well and as expected, in the collection of organic vapors present in air or nitrogen. Obviously a range of compound volatility exists, for which this method is best suited. Depending on a host of parameters--chemical and physical nature of the phase, temperature, sampling rate and volume, dimension of and pressure drop in this cartridge, etc.--hydrocarbons of lower molecular weight will be either insufficiently retarded, or not retarded at all. In the two cartridge approach, this point is signaled by a breakthrough of volatile compounds into the second cartridge. Compounds of still higher volatility will

show similar amounts in both cartridges.

The sampling rates varied between 10 and 30 l/min in different set-ups. Atmospheric tests usually involved 5 to 30 m^3 of air, and the tests using the car exhaust, gasoline, and chlorinated hydrocarbons made use of 0.4 to 2.2 m^3 samples. Judged by gas-liquid chromatography on OV-101, the compounds in the transition region (where breakthrough from the first to the second cartridge occurs) have Kovats indices around 1000 (n-decame).

There is no lower limit of volatility in reference to collection, however, the concentration of organics in vapor form, in the atmosphere, drops off rapidly with increasing molecular weight. Yet, it is perhaps in this area that the method can render its most valuable contribution to pollution problems e.g. when pesticides, certain industrial effluents or polynuclear aromatics, etc., occur in air. Furthermore, it could conceivably be employed in the collection of natural emissions into the atmosphere, e.g. terpenoids from conifers, etc.

Obviously, it is the organics of higher molecular weight which are most difficult to identify, and the described method seems to be one of the best approaches yet to collect enough material for several types of analysis. With so many parameters influencing collection characteristics, the method is flexible enough to be used for a wide variety of conditions and problems.

Chosen from a greater number of chromatograms, four examples may illustrate some of the discussed points. Fig. 4 shows an example of insecticide sampling. The vapor pressure of these chlorinated hydrocarbons is comparatively low; they were consequently completely retained on the first cartridge. Fig. 5 gives an example of car exhaust sampling which the breakthrough region can be clearly observed. Fig. 6 represents an isothermal run of car exhaust with simultaneous use of flame ionization and electron capture detectors, and Fig. 7 compares the profiles of organics sampled in an urban and an industrial area of St. Louis.

Car exhausts was also run on a GC-MS unit and the major peaks identified from their mass spectra. Most of them turned out to be aromatics from toluene to acenaphthene, whose presence in car exhaust, of course is amply documented in the literature. No effort was made to identify all components--which, incidentally, would have been better done with capillary columns and high-resolution photoplate readout.

One intriguing possibility inherent in this approach would be to send cartridges to different locations, where persons interested in the higher organics, present in their respective atmospheres, would need only a pump to draw a suitable amount of air through the cartridge and would then send it back for extraction and analysis. The advantages of one centralized analytical facility, which could survey at low cost any area where a pump and an electrical outlet can be found, are obvious. However, further work on support-bonded phases and their use in the field of air contamination, is definitely needed before plans of these proportions should be seriously entertained.

Collection of Chlorinated Hydrocarbons

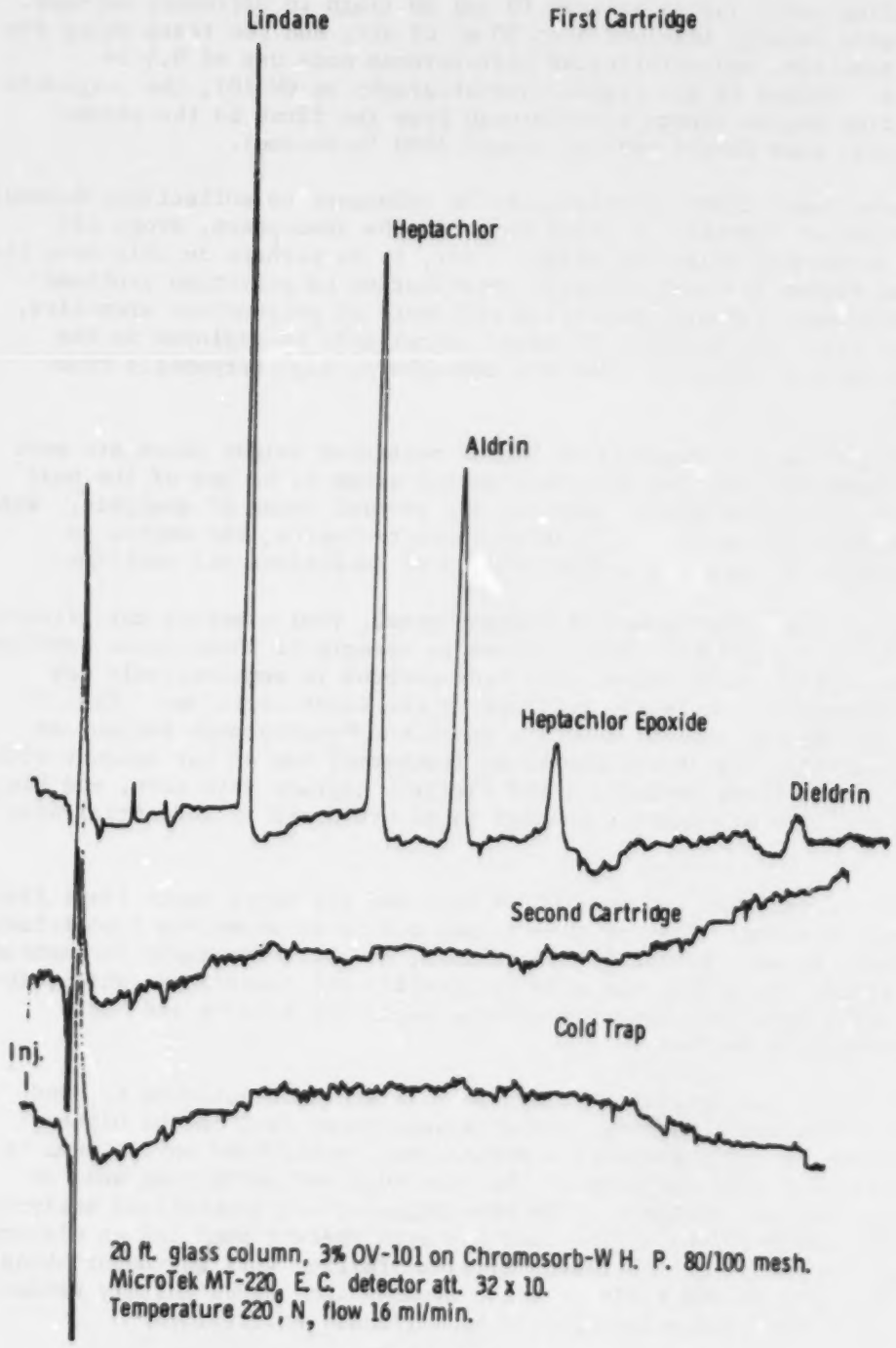
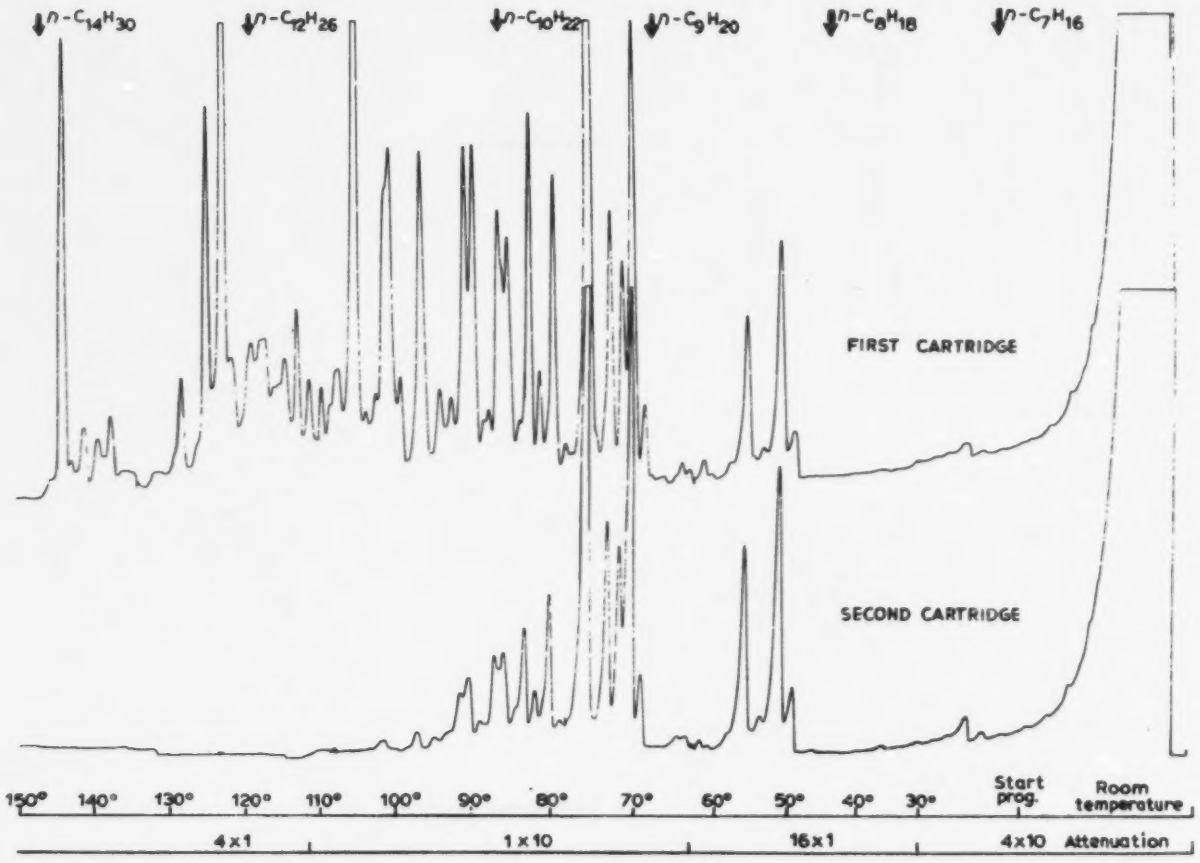
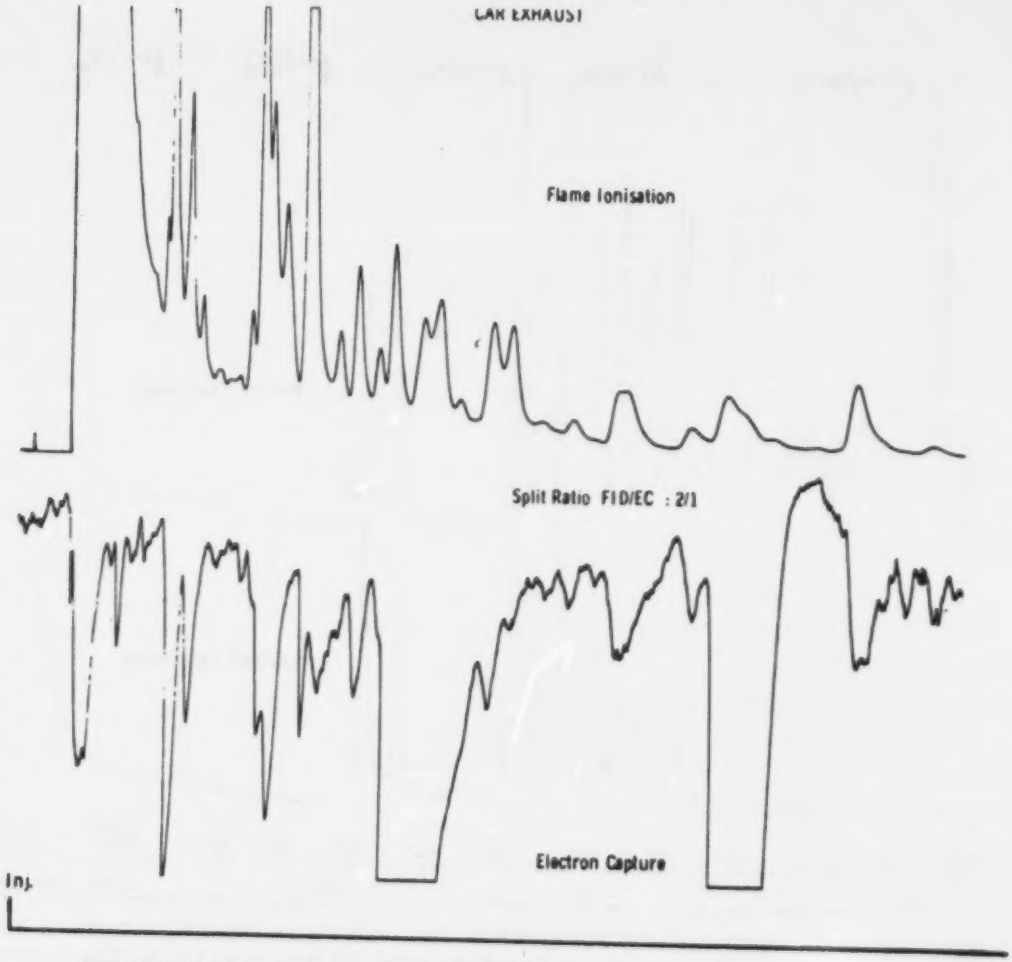


Figure 4



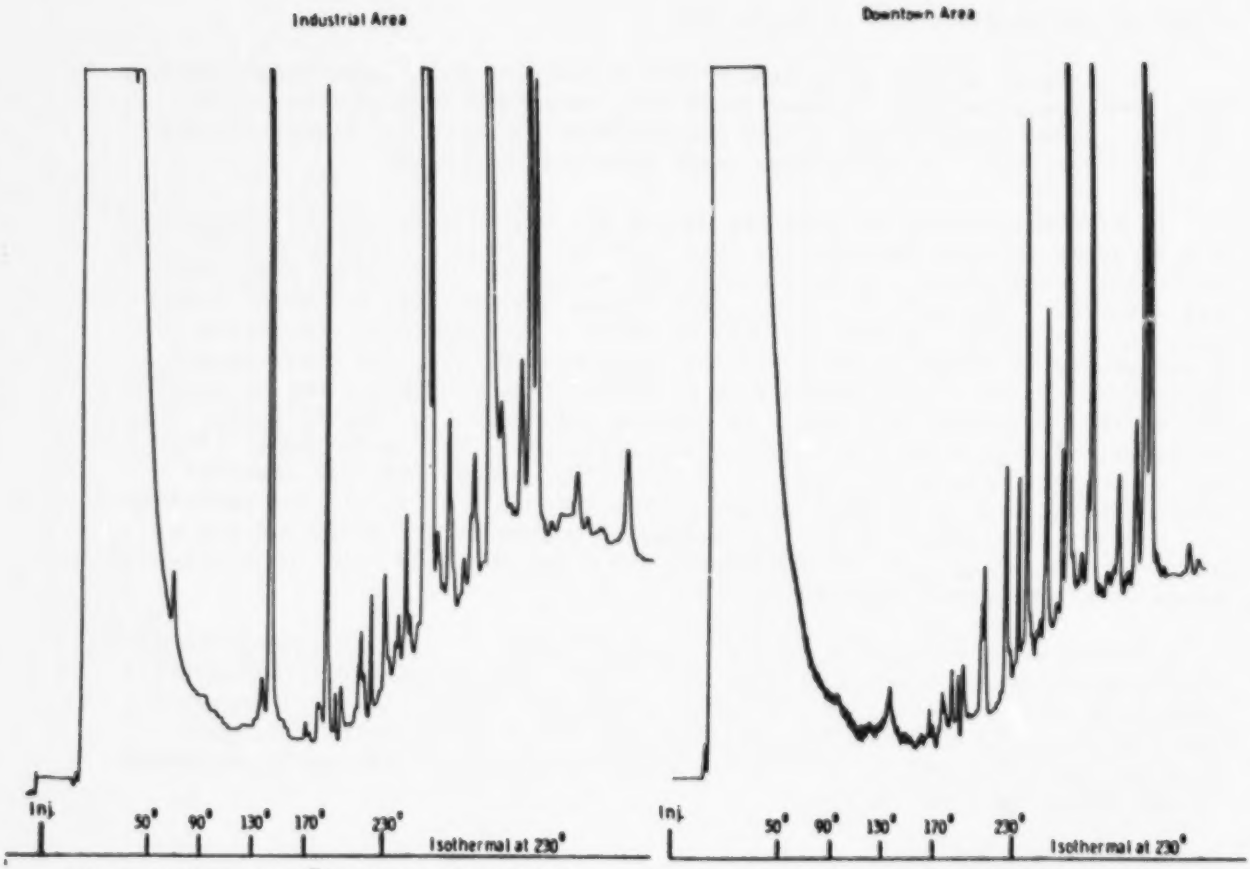
Gas chromatograms of car exhaust components collected on two identical cartridges containing 24 % $[C_{18}H_{37}SiO_{3/2}]_n$ on Chromosorb A. Sampling time, 60 min at 30 l/min. The injections represent *ca.* 0.16 sec of sampling. GC conditions: 3 % OV-101 on Chromosorb W-HP, 80/100 mesh, 20 ft. × 2.5 mm I.D. Pyrex; nitrogen flow optimized, 16 ml/min; flame ionization detector.

Figure 5



2 microliters injection representing 0.54 seconds of sampling. 20 ft. glass column, 3% OV-101 on Chromosorb-W, H.P., 80/100 mesh. Micro Tek MT-220, FID att. 8 X 10, EC 64 X 10. Temperature: 80°. N_2 flow 16 ml/min.

Figure 6



1 microliter injection representing 20.6 liters of air in the industrial area, St. Louis, Missouri. 20 ft. glass column; 2.5 mm i. d. 3% OV-101 on Chromosorb-W, H. P., 80/100 mesh. MicroTek MT-220, FID att. 1 X 8 Program: 10 min. at 50° followed by 8°/min., final hold at 230° N_2 flow 16 ml/min.

1 microliter injection representing 19.6 liters of air in the downtown area, St. Louis, Missouri. 20 ft long column; 2.5 mm i. d. 3% OV-101 on Chromosorb-W, H. P., 80/100 mesh. MicroTek MT-220, FID att. 1X 8 Program: 10 min. at 50° followed by 8°/min., final hold at 230° N_2 flow 16 ml /min.

Figure 7

MODIFIED ADSORBENTS BASED ON SILICA GEL

Silica gels are the most widely used adsorbents for column chromatography. This preference prevails because these materials have large surface areas, diverse surface activities, easily controllable porosity and finally because they are available in narrow-size range spherical particles.

A systematic study of treating silica gel (60/80 mesh) in the presence of liquid water at high temperatures (hydrothermal treatment) was done under more controlled conditions. In this controlled study, an interesting phenomenon was observed: The plot of surface area versus hydrothermal treatment temperature gave a minimum at the vicinity of 300°C. Although this controlled procedure is in someway similar to that done earlier (3), the early experimentations did not show a minimum up to 380°C. The difference may be attributed to the pronounced difference in cooling rate which in turn influence the redeposition of silica. The early work used a small Parr Bomb (Model 4740) and under the experimental conditions, a 5-hour cooling time was observed after removal from an unthermostated muffle furnace; the controlled method in the present experiments used a big volume Parr Bomb (Model 4652) and had a 1.5-hour of cooling time after removal from a thermostated bath; both after 18 hours of hydrothermal exposure.

The apparent similarity in the two hydrothermal treatment procedures gave different results. Kiseley, et al. (4), Unger, et al. (5) and Kirkland (6) described various methods of preparing silica gel. It is now well accepted that the man-made silica gel commands a wide range of surface areas, pore volumes, distributions and sizes, all these properties being highly dependent on the method of preparation.

Results and Discussion

Figure 8(a) and 8(b) show the effect of hydrothermal treatment with surface areas produced by both methods. Fig. 9 shows the retention temperatures of octane and hexadecane on different surface area silica gels shown on Fig. 8(b). As expected, the uncoated silica gel shows decrease retention temperatures with decrease surface area. In the GC testing of still lower surface area, uncoated silica gels, (equivalent to greater than 300°C HT), results seem to indicate an upturn to increasing retention of hydrocarbons and alcohols. To speculate, this could be a change to a more active surface of the gel.

More important perhaps--this study demonstrated that the silica gels obtained by both methods around the critical temperature of water, surprisingly, can bond very thick layers of polymers. Typical examples of this very interesting and potentially useful observation is shown on Fig. 10 with Carbowax 20M and OV101. Thus, as the surface area decreases, the decreasing contribution to the retention of the absorption process is made up for, in part, by the increasing contribution of partition in the thickening polymer layer. This is the reason that coated, low surface-area silica gels do not lose, to any great degree, their ability to retain organics as blank silica gels do.

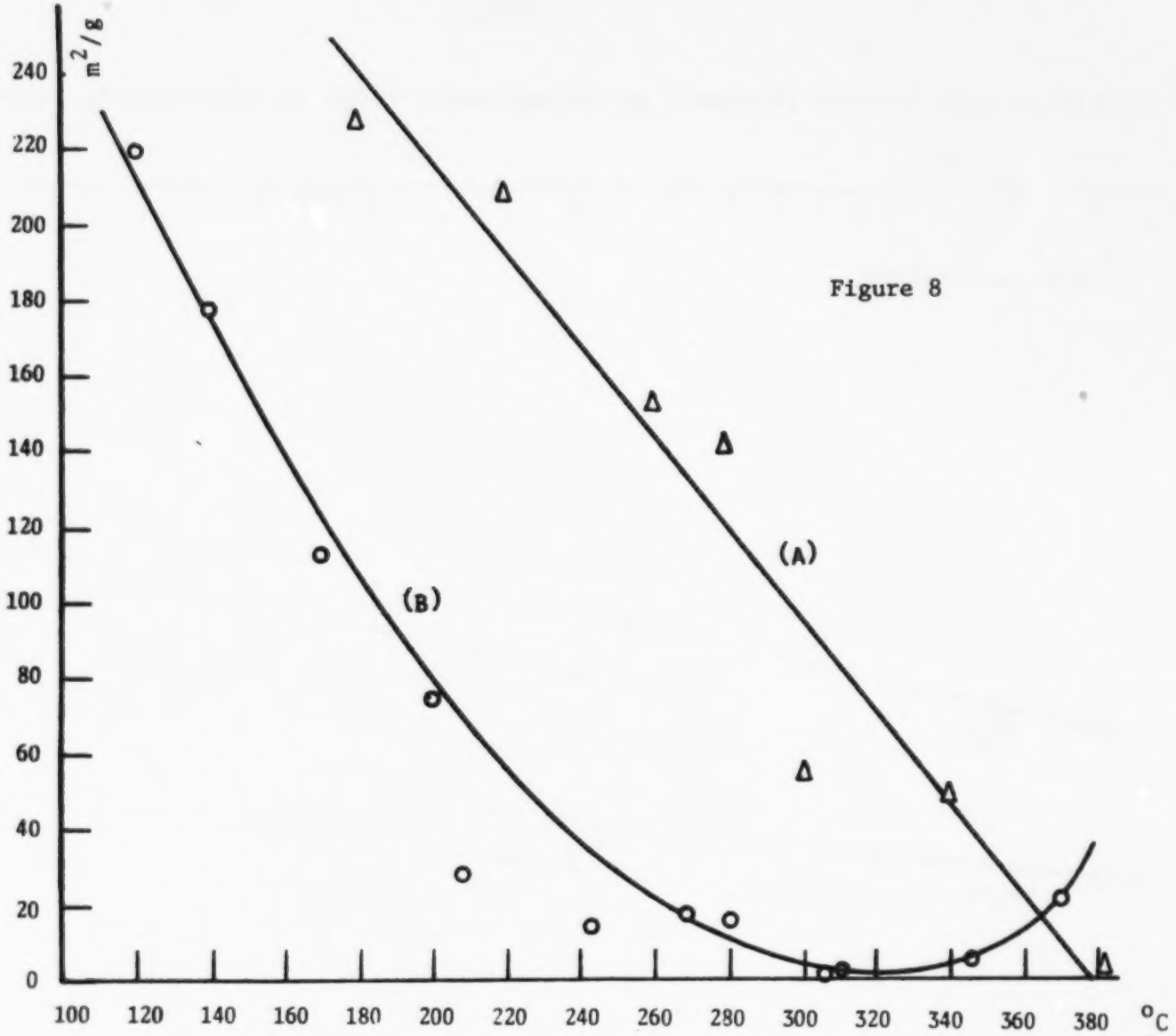
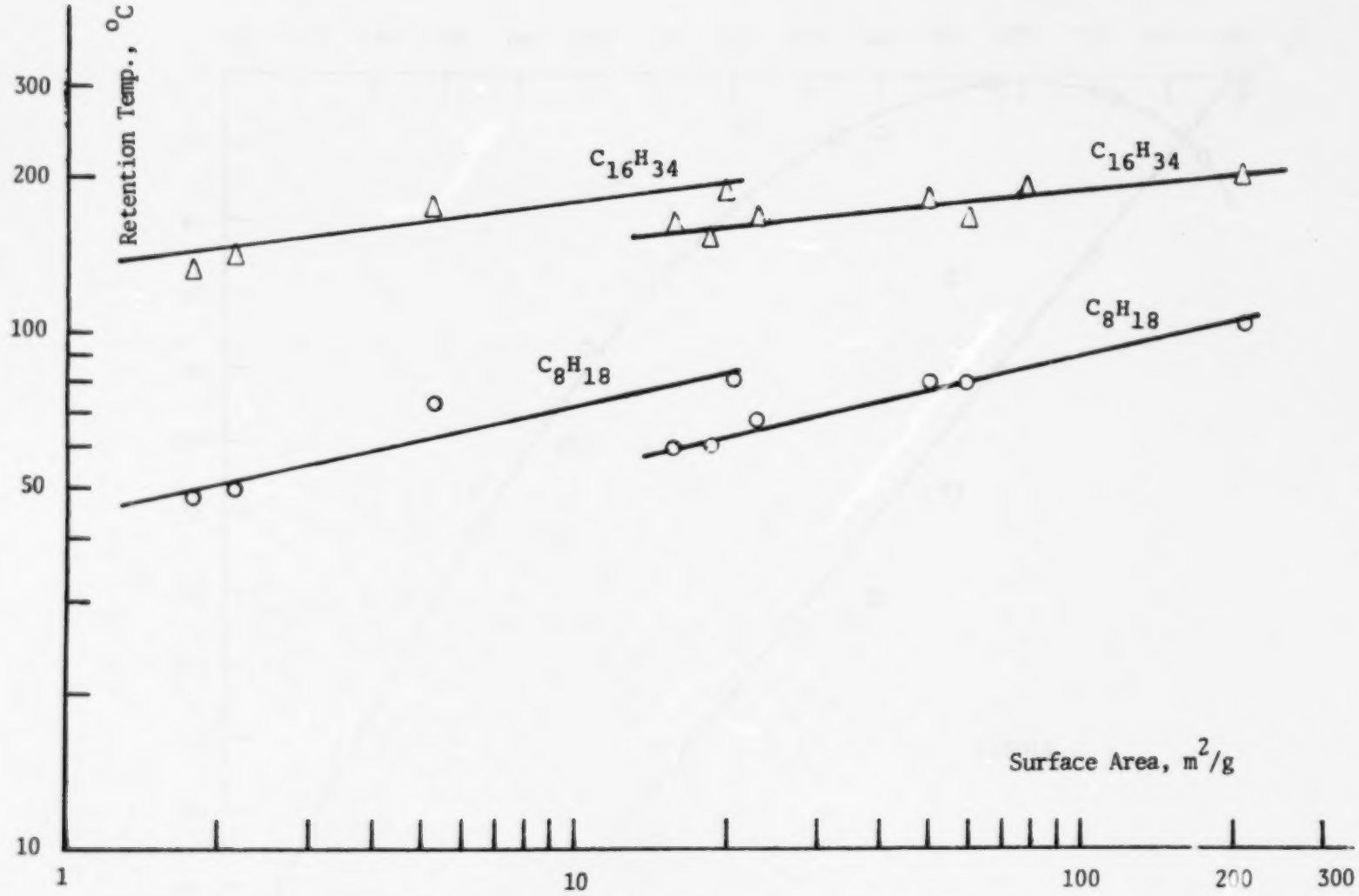


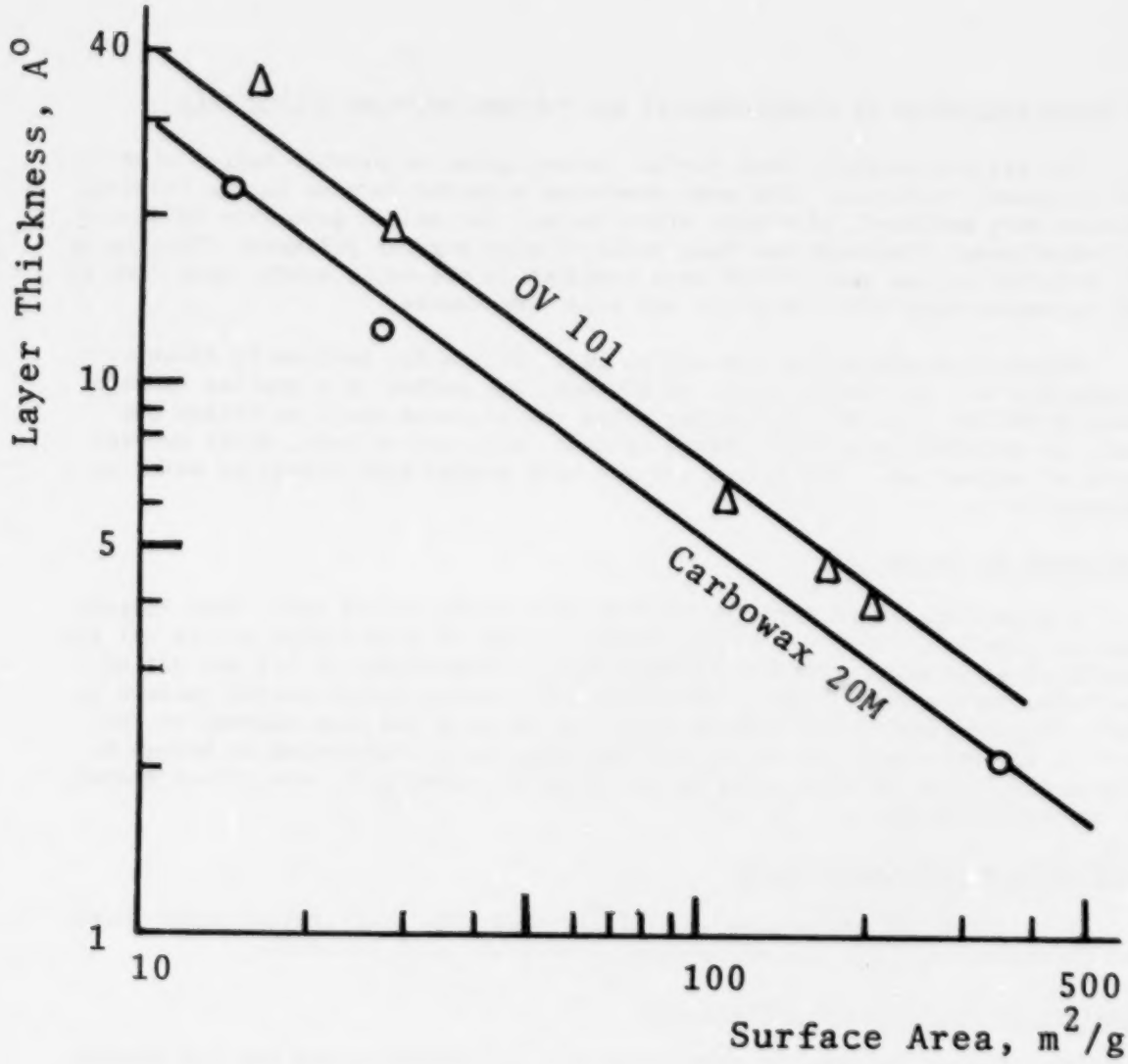
Figure 8

SURFACE AREA OF DAVISON SILICA GEL 62 AS A FUNCTION OF HYDROTHERMAL TEMPERATURE. (A) REF. 3 (B) THIS STUDY, TO BE PUBLISHED.



RETENTION TEMPERATURES OF MODEL HYDROCARBONS ON DIFFERENT SURFACE AREA SILICA GELS.

Figure 9



Thickness of non-extractable layers of organic polymers on hydrothermally treated silica gel.

Figure 10

GC CHARACTERIZATION OF HYDROTHERMALLY AND POLYMER MODIFIED SILICA GELS

The silicic supports were further investigated to provide better stability and increased retention. The most promising supports as seen in the previous section were modified, wide pore silica gels. The silica gels were subjected to hydrothermal treatment and then modified with organic polymers. Testing of the modified silica gels, which were prepared in the early study, were done by gas chromatography with non-polar and polar substances.

General preparation of the silica gel: Silica Gel Davison 62 (Fisher Scientific Co., St. Louis, Mo.), 40-60 mesh, was washed in a Soxhlet (Kontes Model K-585100) with HCl at boiling point temperatures until no yellow hue could be detected in a fresh charge of conc. HCl, hot or cold, after several hours of extraction. The silica gel was then washed with distilled water to neutrality.

Hydrothermal Treatment

A high-temperature bomb (Model 4740 with Pyrex insert tube, Parr Instrument Co., Moline, Ill.) was filled with a slurry of acid-washed silica gel and distilled water such that their levels were at approximately 2/3 and 3/4 of the tube, respectively. The closed bomb was lowered into a muffle furnace at 280°, left overnight, and removed after the furnace had been allowed to cool down in the morning. The silica gel was then again acid-washed as before to remove any traces of metal originating from the steel bomb, its nickel gasket, or copper lubricant.

Modification with Carbowax 20M

Dry silica gel was coated with 6% Carbowax 20M, heat-treated under nitrogen overnight at 260°, and exhaustively extracted with methanol.

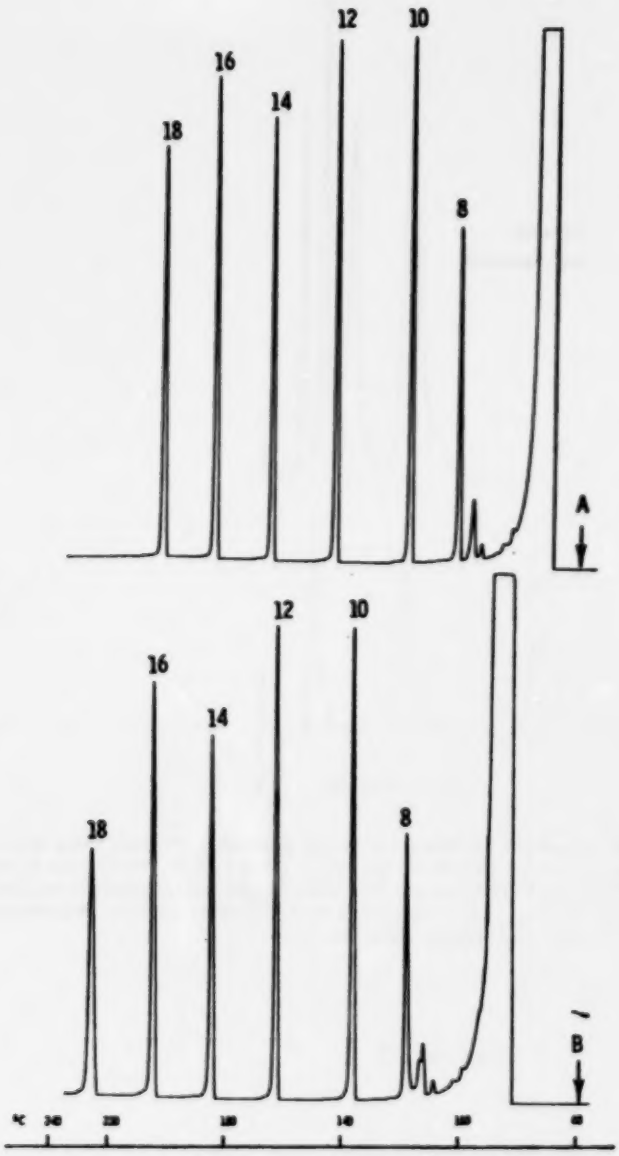
Addition of Water to the Carrier Gas

The carrier gas line of a Microtek-220 gas chromatograph was cut between flow-control module and injection port, and the nitrogen made to bubble through distilled water contained in a stainless-steel trap.

Results and Discussion

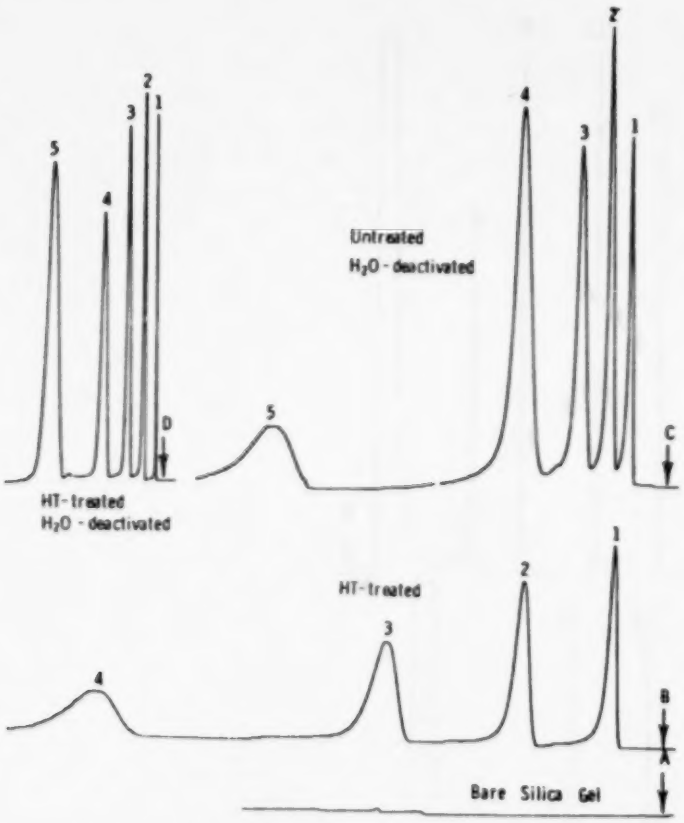
The hydrothermal treatment at 280°C reduced the surface area of silica gel considerably (to 141 m^2/g. Micromeritics Instrument Corp., Norcross, Ga.). The non-extractable coating of Carbowax 20M on this support had a nominal thickness of 2 Å (carbon 1.52%, Peninsular Chemical Research).

Acid-washed Silica Gel 62, without the benefit of further modifications, gave good chromatograms of n-hydrocarbons (Fig. 11). It failed to pass any alcohols, however, at 140° (Fig. 12, trace A). This separation must be obtained



Separation of even-numbered *n*-alkanes (octane through octadecane) on bare silica gels. Both columns: Silica Gel 62, 40–60 mesh, acid washed; in 120 cm × 4 mm I.D. Pyrex U-tube, nitrogen flow-rate 80 ml/min, 6 °/min temperature program, FID. (A) Silica Gel 62 hydrothermally treated at 280° overnight and acid washed; (B) untreated silica gel. The *n*-alkanes are represented by their number of carbon atoms.

Figure 11



Separation of n-alkanol standards (methanol through pentanol) on bare silica gels. All columns: Silica Gel 62, 40–60 mesh, acid washed; in 120 cm × 4 mm I.D. Pyrex U-tube at 140°, nitrogen flow-rate 80 ml/min, FID. (A) Bare silica gel; (B) Silica Gel 62 hydrothermally treated at 280° overnight and acid washed; (C) carrier gas saturated with water at ambient temperature; (D) water-deactivated and hydrothermally treated silica gel.

Figure 12

by either hydrothermal treatment (Fig. 12, trace B), or coating with Carbowax 20M (Fig. 13, trace D), or the presence of water in the carrier gas (Fig. 12, trace C). Other traces show various combinations of the three treatments, all tested under the same chromatographic conditions.

GC of lower aliphatic alcohols provides in our opinion a severe test for the degree of deactivation of the adsorbent surface. Each of the methods did well on its own--combining all three of them (Fig. 13, trace A) may have been detrimental (at least in this particular analysis), but was included to allow a visual comparison of effects accumulating under the same chromatographic conditions. Fig. 14 represents a more reasonable choice of parameters for the separations of the alcohols, i.e. a temperature-programmed run without the benefit of water in the carrier gas.

Judging from the chromatographic improvement obtained by the use of these three simple techniques, it would appear feasible to modify silica gels further (e.g. by further reduction of the surface area combined with the use of better monomolecular layers) to a point where they can be used in place of diatomaceous supports.

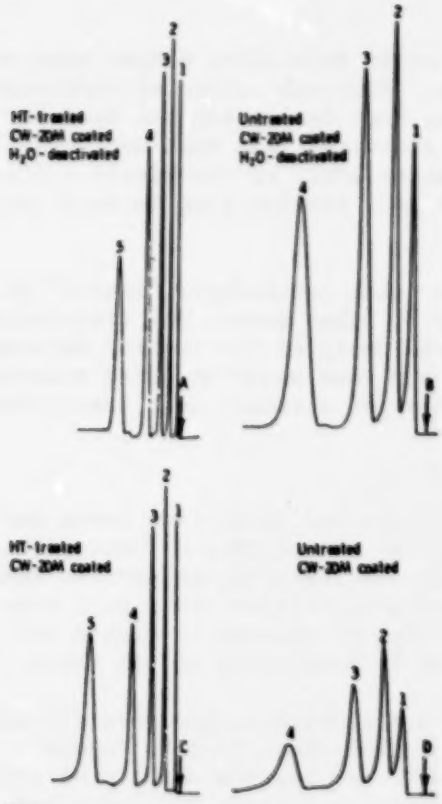


Fig.13

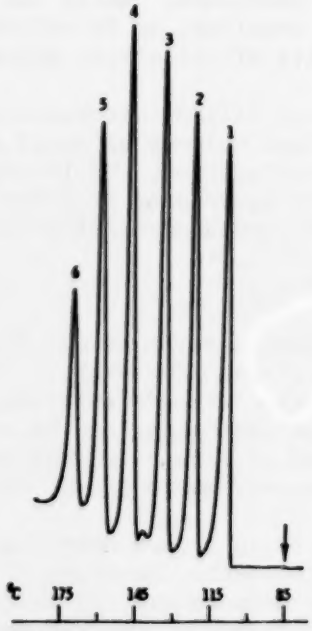


Fig.14

Fig. 13. Separation of n-alkanol standards (methanol through pentanol) on Carbowax-coated silica gels. All columns: Silica Gel 62, 40–60 mesh, acid washed, coated with Carbowax 20 M, heat-treated and extracted; in 120 cm × 4 mm I.D. Pyrex U-tube at 140°, nitrogen flow-rate 80 ml/min, FID. (A) Silica Gel 62 hydrothermally treated at 280° overnight and acid washed (before coating with Carbowax), carrier gas saturated with water at ambient temperature; (B) water-deactivated silica gel; (C) hydrothermally treated silica gel; (D) untreated silica gel.

Fig.14. Separation of n-alkanols (methanol through hexanol). Column: Silica Gel 62, 40–60 mesh, acid washed, HT-280°, coated with Carbowax 20 M; in 150 cm × 2 mm I.D. Pyrex U-tube, nitrogen flow-rate 80 ml/min, temperature program 6°/min, FID.

Figures 13 & 14

A GAS CHROMATOGRAPHIC CARTRIDGE DESORPTION PORT

In the course of studies on the efficiency of solid media for the collection of trace vapors in the atmosphere, it became necessary to divise a suitable cartridge system for sample acquisition, transport and introduction into a gas chromatograph for analysis.

The collection media to be tested were solid materials, either bare or with a polymer layer bonded to their surface. Although collected compounds could be removed easily by liquid extraction, heat desorption was used for the purposes of this study: it is faster, more sensitive, and much more prone to decompose collected compounds. While the latter would be considered a disadvantage in actual sampling, it is valuable in a testing program to establish the catalytic activity of collection phases.

These phases were filled into stainless steel cartridges, "loaded" by drawing through defined volumes of doped air or other gases, and transferred to the GC introduction system. The latter was designed for testing several variants of a finally envisioned procedure, and thus wound up being somewhat more complex than one would consider necessary for straight heat desorption.

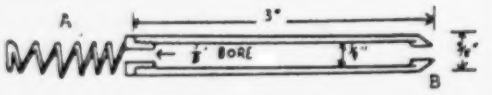
Results and Discussion

Fig. 15 shows some details of the collection and desorption ports and Fig. 16 a schematic of the flow system. The two valves (Valco Instruments, Houston, Texas) and the lab-made cartridge desorption port can perform several functions. A "loaded" cartridge can be swept with carrier gases at a wide range of temperatures or flow rates and can also be completely closed off; while the carrier gas stream to the GC column is maintained at all times.

This can serve to introduce only desired retention ranges from a loaded cartridge into the GC system (position A) and vent other (B); to "clean" cartridges at higher temperature (b) and then check for the absence of artifacts (A); to heat a directly injected sample or an externally loaded cartridge in a closed-loop position (C and D) and then release the vaporized compounds cum decomposition products suddenly into the GC system (A); to study the influence of various parameters on analytical accuracy; to inject directly into a cold or hot cartridge or the GC column (C, A, B), and so forth. Needless to say that the principles of these approaches have been well known in gas chromatography; with examples too numerous to cite.

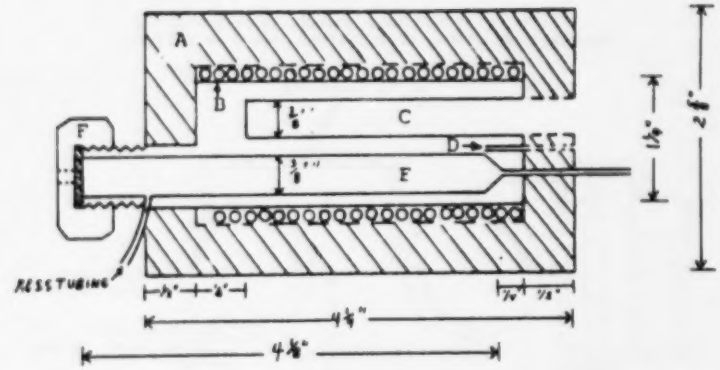
Both port and valves are contained in an aluminum box with thick bottom heated by cartridge heaters and surrounded by Marinite insulation. The cartridge port is, in addition, independently heated by a cartridge heater, or cooled by a flow of water or carbon dioxide. It is also thermally insulated. The whole arrangement is situated close to the regular injection port of the gas chromatograph, with thermal configurations designed to avoid any cold spots in connecting lines.

Aside from laboratory testing, the system can be used for straight field sampling and subsequent cartridge transport to the laboratory. Sample streams

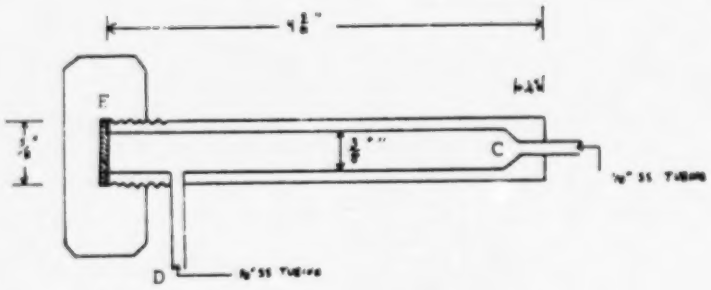


STAINLESS STEEL COLLECTION CARTRIDGE

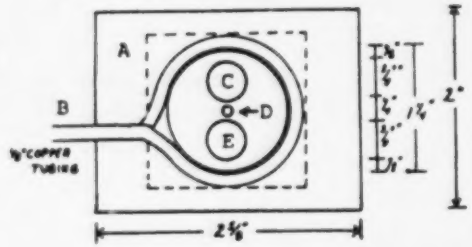
ALUMINUM DESORPTION PORT



CROSS SECTION



STAINLESS STEEL CARTRIDGE HOLDER

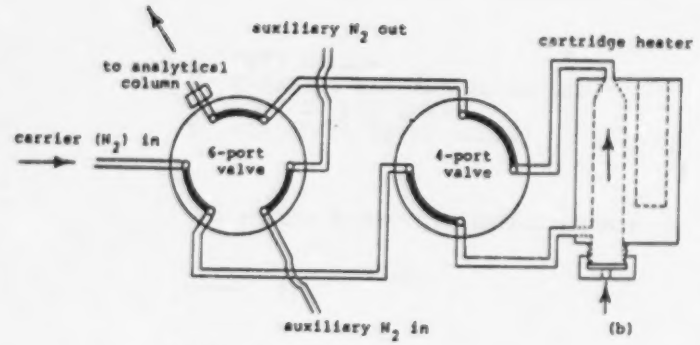


A STAINLESS STEEL SPRING
B CONE TO FIT SEAT C
D SAMPLING STREAM, IN OR OUT
E LEAD SEPTUM

A MARINITE INSULATION
B COOLING COILS
C FOR HEATING CARTRIDGE
D FOR THERMOCOUPLE
E FOR COLLECTION CARTRIDGE
F SEPTUM, LEAD OR SILICONE RUBBER

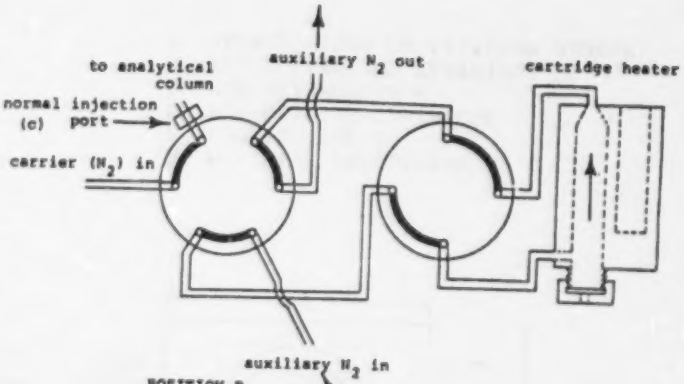
Collection cartridge, holder and desorption port.

Figure 15



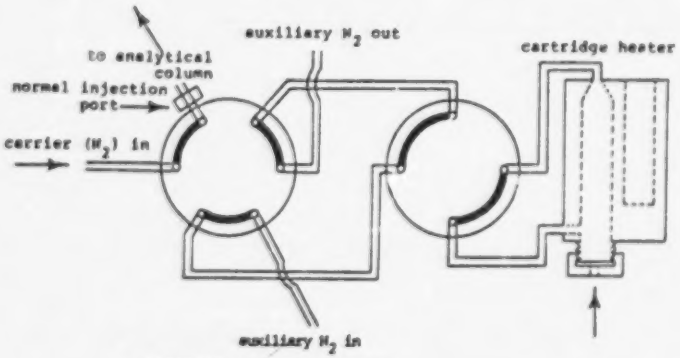
POSITION A

(a) HEATING OF LOADED CARTRIDGE, DISCHARGE TO GC
(b) DIRECT INJECTION THROUGH HOT CARTRIDGE



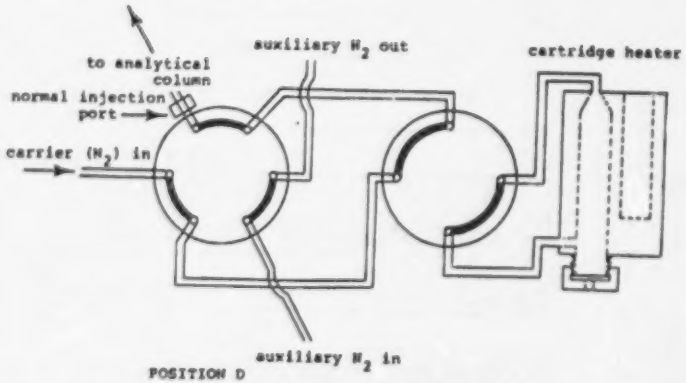
POSITION B

(a) CLEANUP OF CARTRIDGE
(b) REMOVAL OF SOLVENT
(c) DIRECT INJECTION TO GC



POSITION C

DIRECT INJECTION TO COLD CARTRIDGE



POSITION D

HEATING OF LOADED CARTRIDGE IN CLOSED-OFF POSITION (DISCHARGE TO GC THROUGH POSITION A)

Flow patterns of the valving system with some typical uses.

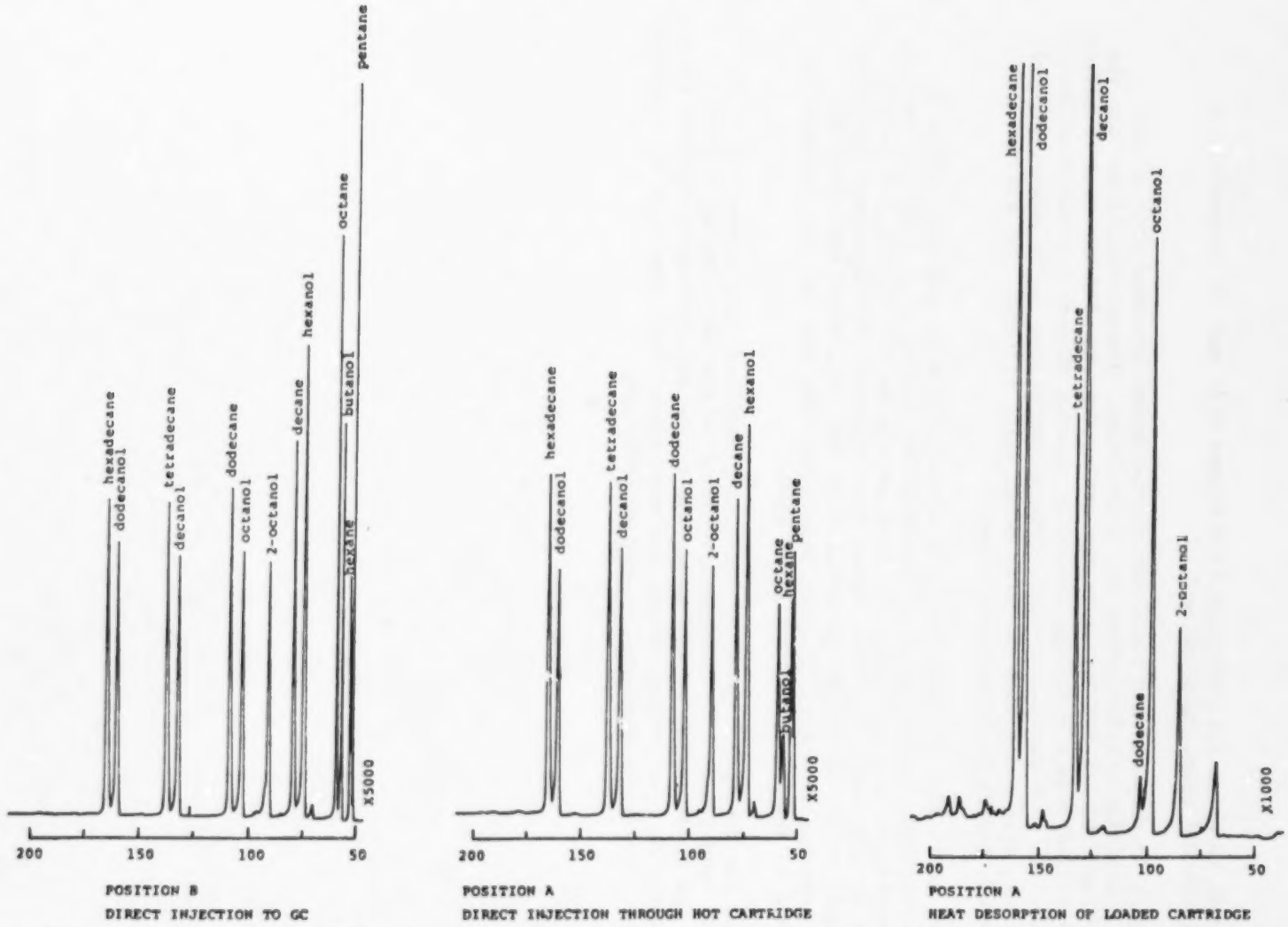
Figure 16

can be made to enter the cartridge from either side and, if necessary, at temperatures different from ambient.

Figure 17 shows some typical gas chromatograms obtained with a text mixture containing n-hydrocarbons and n-alcohols. Direct injections into the GC column and through the hot cartridge are contrasted with two runs involving heat desorption from a cartridge loaded by drawing through a greater volume of doped air. In this particular case, some decomposition of the higher alcohols is apparent, with collection cut-offs being quite different for alkanes and alkanols of comparable GC retention time.

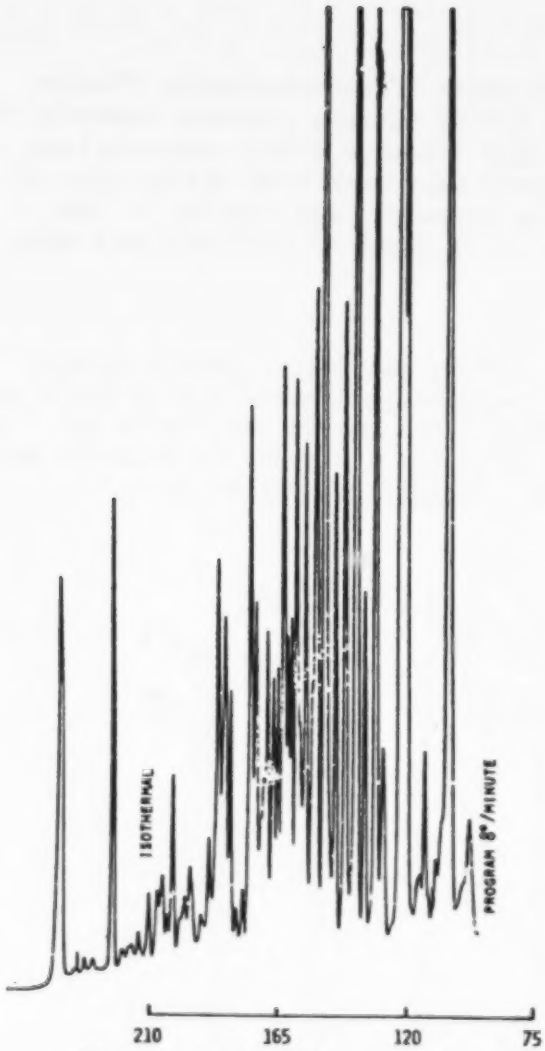
Here as in Fig. 18, which shows a typical run with gasoline vapors in air, the cartridge contained a surface-modified silica gel. After collection, it was heated in the cartridge port from ambient to 230° in ca. 2.5 minutes and left at that temperature for three more minutes. The vaporized compounds were routed to the GC column (position A in Fig. 16), which was close to ambient temperature during the heat desorption step and was then temperature programmed to obtain the chromatograms shown.

When the desorption port was initially installed, the valves had to be carefully conditioned (i.e. frequent rotation of the valve during initial heat-up and conditioning at 300° according to the manufacturer's instructions) to prevent them from getting stuck, and some minor leaks developed on occasion. Otherwise, the system performed to our satisfaction.



Chromatographic comparisons of different sample introductions to the valving system. Conditions: injected, 1 μl of alcohol–hydrocarbon mixture: initial temperature, 50°; program rate, 8°/min; temperature FID, 225°; analytical column, 3% OV-17 on Chromosorb W, 100–120 mesh, 6 ft. × 2 mm I.D. borosilicate glass.

Figure 17



Chromatography with the introduction flow pattern as shown in position A of Fig. 2. 10-min collection in atmosphere enriched with gasoline vapors. Solid adsorbent is hydrothermally treated (210°) silica gel 62 modified with non-extractable layers of OV-101. Temperature: multiport introduction system, 190°; FID, 225°. Analytical column: 10% FFAP on Chromosorb W, AW DMCS, 80-100 mesh, 20 ft. × 2 mm I.D. borosilicate loop tube. Attenuation, · 2000.

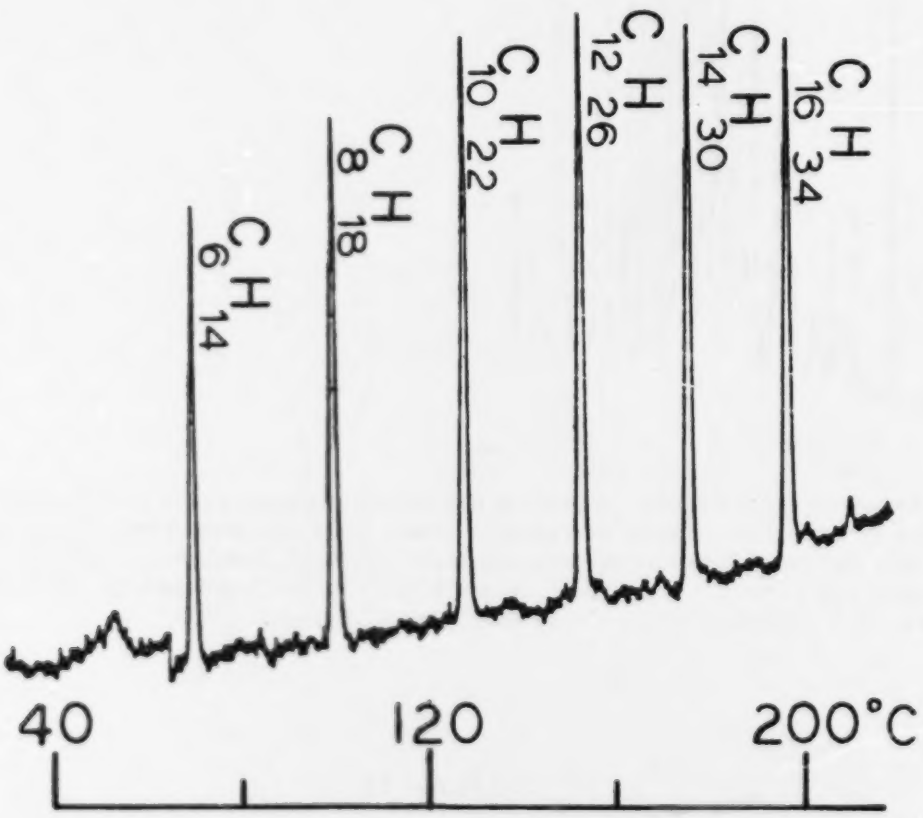
Figure 18

OTHER POLYMER MODIFIED SILICA GELS

The success obtained with the modification of hydrothermally treated silica gels with Carbowax 20M led to the use of various polymers commonly used as liquid phase in gas chromatography. This included linear polyethylene, AN-600, ON 870, FFAP and SE-30. These polymers were used with silica gels of different surface areas. The modification procedure was similar to that described in the previous section. A total of about 40 packings were made.

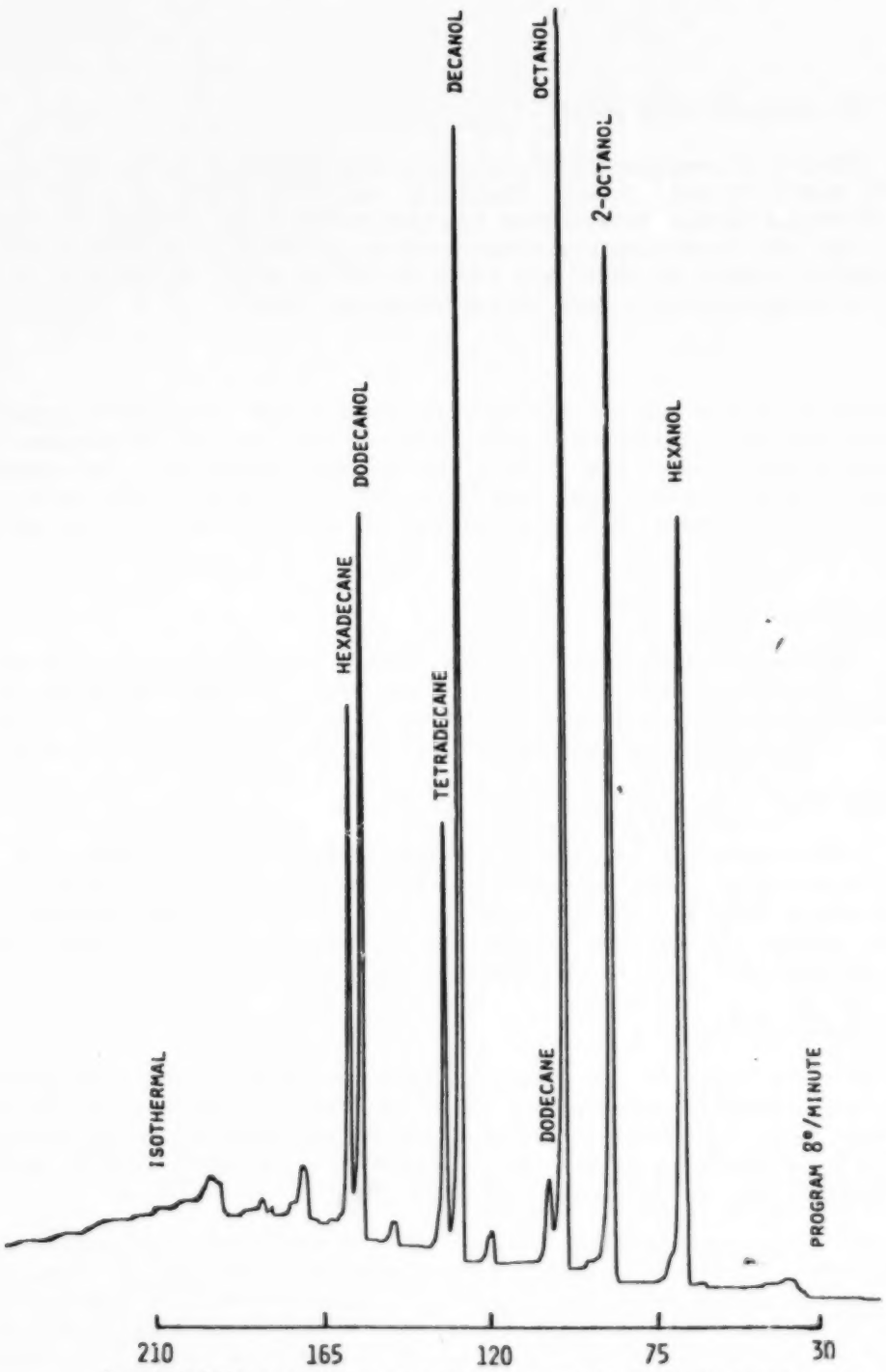
Results and Discussion

In the gas chromatographic testing (dry N_2 as carrier gas) alcohols (butanol) do not elute on silica gel hydrothermally treated around 200°C or below even modified with an organic polymer (for example see Figure 19). The packings were also tested as collection media for a mixture of alcohols and hydrocarbons pumped out of teflon bag (for example see Figure 20).



Gas chromaotgram of hydrocarbons on silica gel, hydrothermally treated at 210°C and modified with non-extractable layers of OV 101.

Figure 19



1 MICROLITER ALCOHOL-HYDROCARBON MIX INJECTED TO 28 LITER N_2 IN TEFLON BAG, CONTENTS PUMPED OUT IN 70 MINUTES; SOLID ADSORBENT IS HYDROTHERMALLY TREATED (210°) SILICA GEL 62, MODIFIED WITH NON-EXTRACTABLE LAYERS OF OV 101; TEMPERATURE MULTIPORT INTRODUCTION SYSTEM 190°; TEMPERATURE FID 225°; ANALYTICAL COLUMN IS 3% OV 17 ON CHROMOSORB W 100/120; x1000; 6 FT X 2 MM ID BOROSILICATE U-TUBE

Figure 20

HUMIDITY AND SAMPLING FLOW RATES

The effects of sampling flow rates and high humidity on the various solid collection media are well known. Therefore, selected silica gels carrying a variety of bonded layers were tested for the presence and absence of these effects. The most promising cartridge packing appeared to be silica gels hydrothermally treated at 208°C and 280°C (4 and 30 m^2/g) modified with thick layers of non-extractable linear polyethylene and OV101.

Dry Air

A 28-liter teflon bag was filled with dry air and spiked with alcohol-hydrocarbon mixture. The bag was left under a heat lamp for 20 minutes to insure homogeneous vapor state, before the bag was pumped out. The experiment was repeated for each packing at four different flow rates. Flow rates between 20 and 200 cm/sec (0.4 to 4 liters/min) were tested. Silica gel mesh size was 25/40.

Moist Air

The compressed air from the tank was slowly bubbled through a water container then used to fill a 28-liter teflon bag. The bag was spiked with the alcohol-hydrocarbon mixture and left as before for 20 minutes under a heat lamp. Four experiments were performed at four different flow rates.

Heat Desorption

The loaded cartridge in each of the experiments described above was analyzed immediately after collection. The alcohols and hydrocarbons trapped in the cartridge were released by heat desorption (see previous section) to an analytical column. The GC conditions were 3% OV17, FID at 230°, inlet 210°, transfer line of 215° and valves temperature of 250°C.

Results and Discussion

Based on the data, it can be generalized that none of the four systems tested showed a significant decrease in collection efficiency as a function of flow rates. It is therefore possible to use a high sampling speed with a particular cartridge with little regard to humidity, support surface area, or type of bonded (unpolar) polymer.

Figures 21-26 summarize the effects of flow rates and humidity on the collection efficiency. Typical GC chromatograms for this type of sampling is shown on Figures 27(a) and 27(b) from which Figures 21-24 were deduced. Generally the effects of different levels of humidity were small, and noticeable only with compounds at the border of the collection range. The retention of alcohols on polyethylene showed, if anything, a slight improvement in moist atmosphere. Hydrocarbons under the same conditions did worse. On polysiloxane both alcohols and hydrocarbons did somewhat worse under moist conditions, but the effects, as stated above, were quite small.

The effect of surface area on retention was as predicted in direction, but not in magnitude. The lower surface area silica gels did collect less of the "border-case" compounds--but the effect was quite small. This is most likely caused by the thicker polymer layers being found on the silica structures with the widest pores.

The effect of surface area on decomposition rates of higher alcohols during heat desorption at ca. 250°C was again predictable and small--the low surface area material inducing somewhat less decomposition. Under conditions of solvent extraction, of course, one would not expect any decomposition at all. Even under the trying conditions of heat desorption, however, the extent of decomposition was generally small.

Figures 28-30 simply show some examples of samplings in doped atmosphere in 5, 10 and 15 minutes of collection.

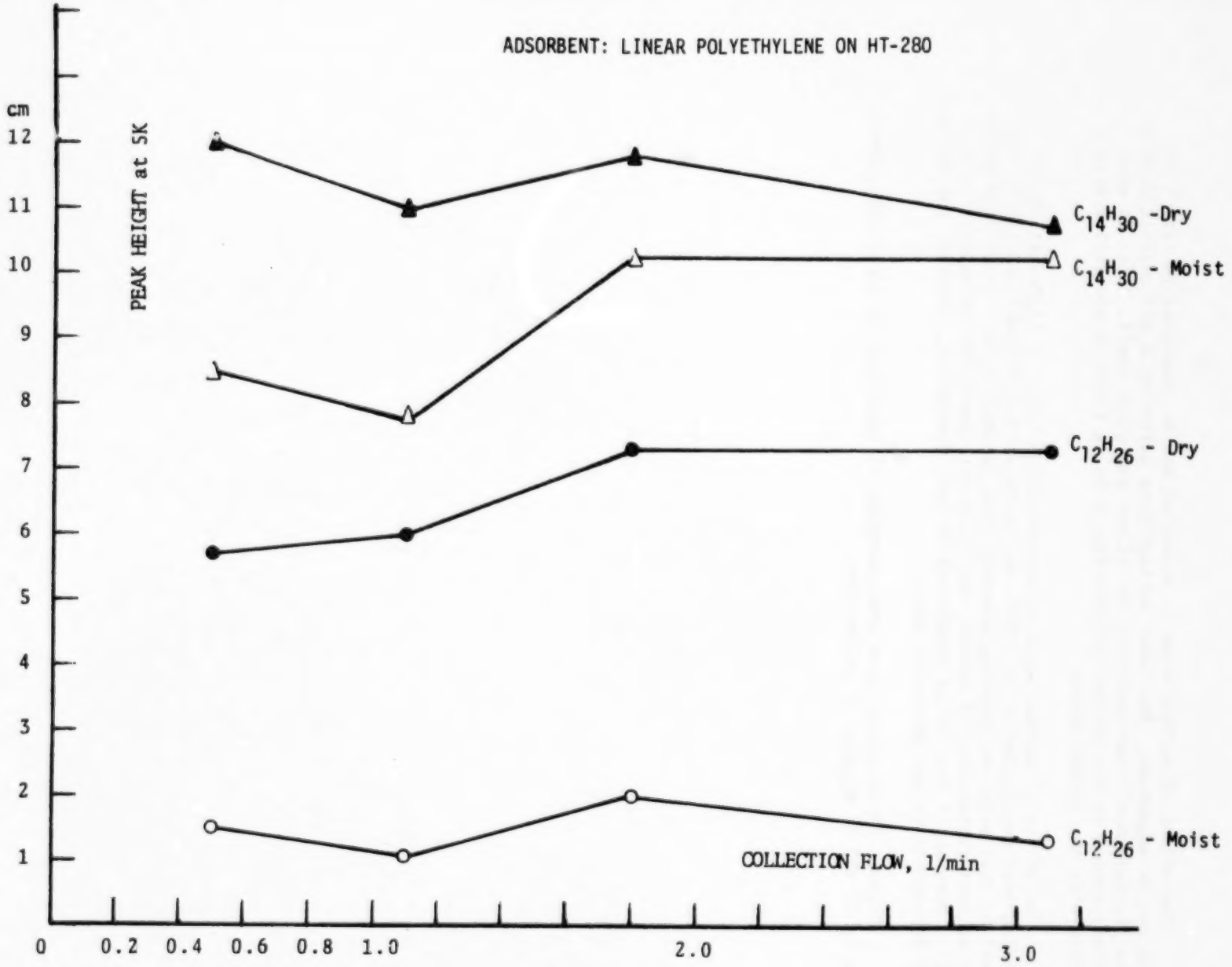
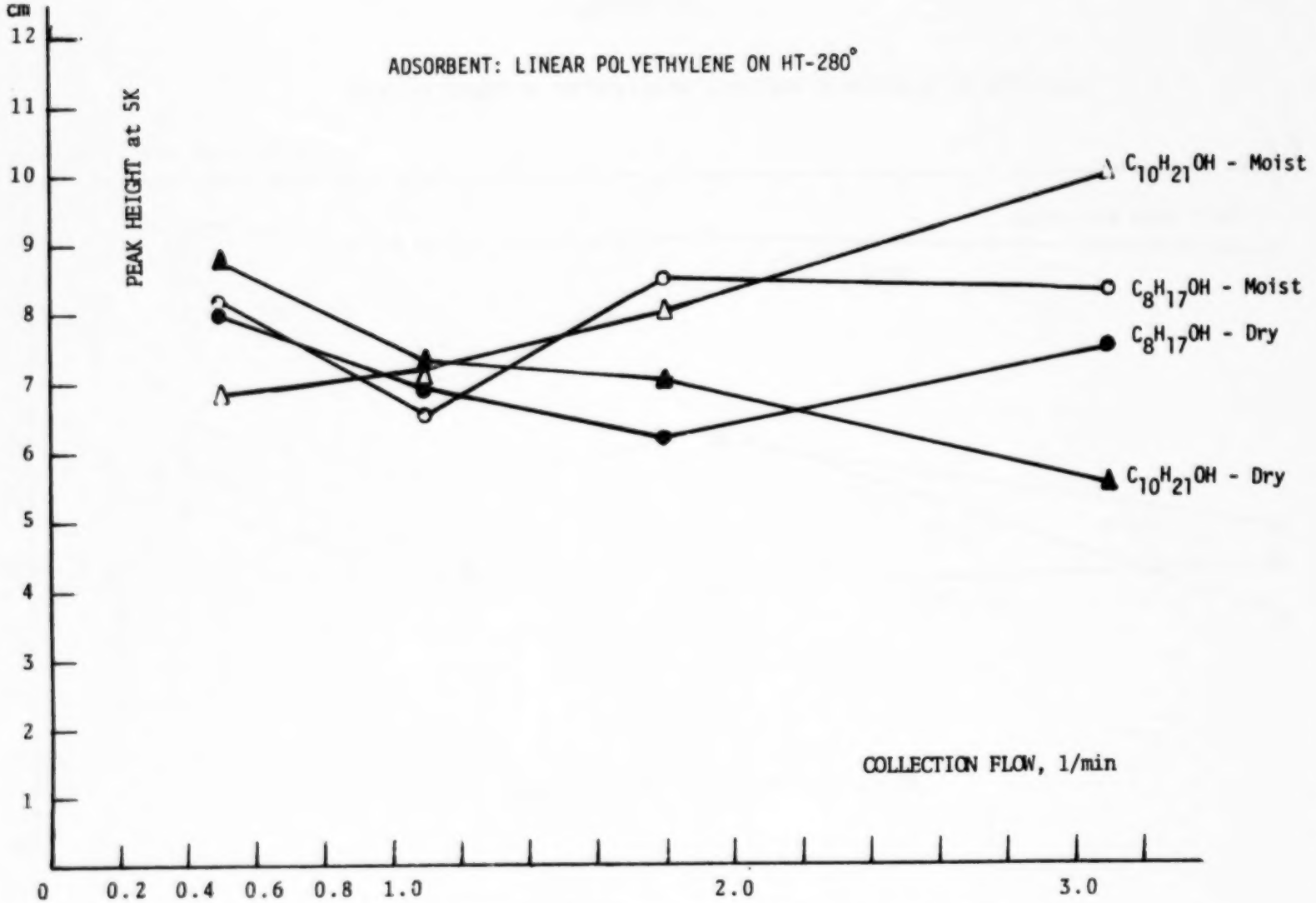
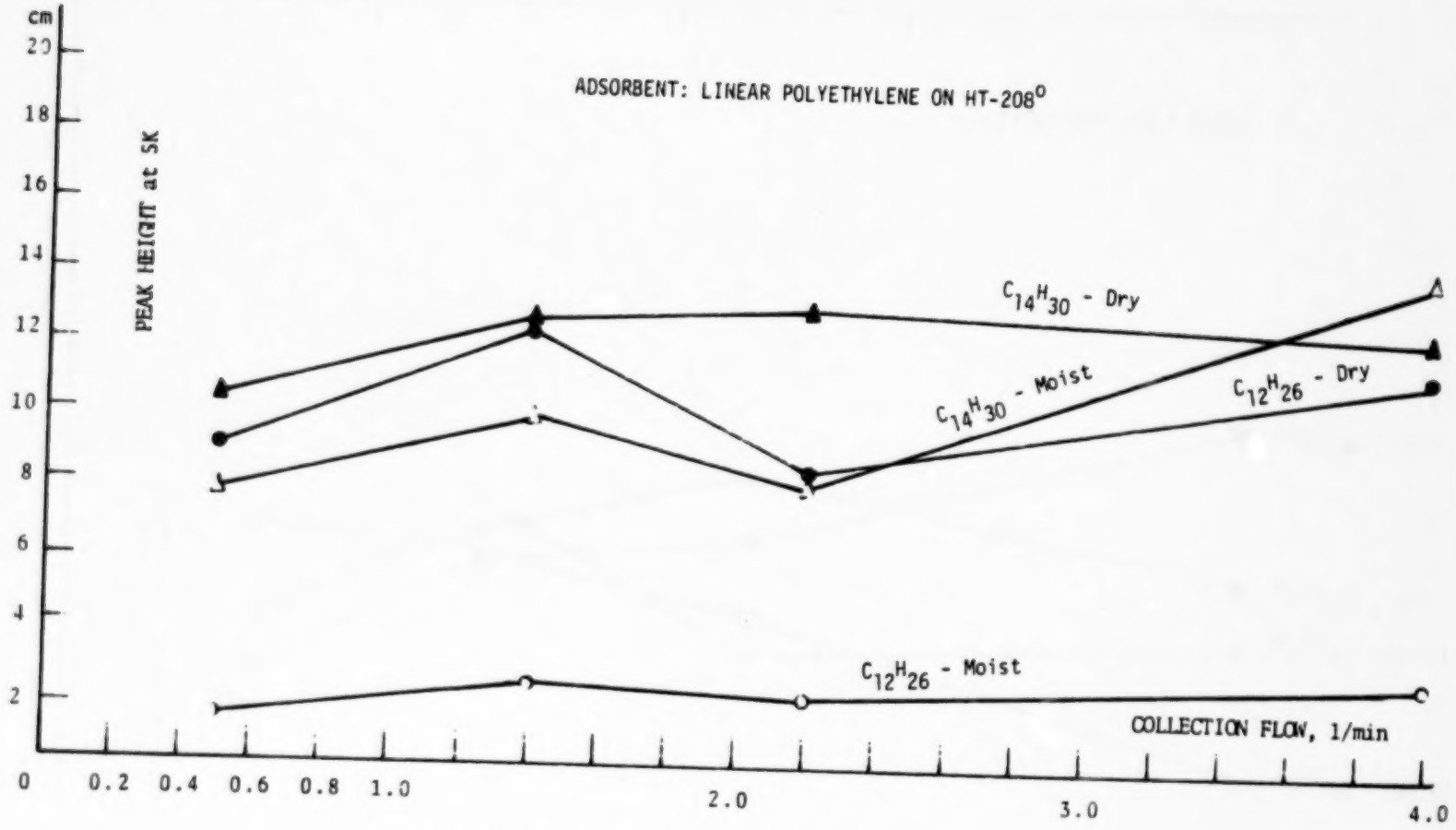


Figure 21 RELATIVE DEGREE OF COLLECTION AS FUNCTIONS OF HUMIDITY AND FLOW RATES



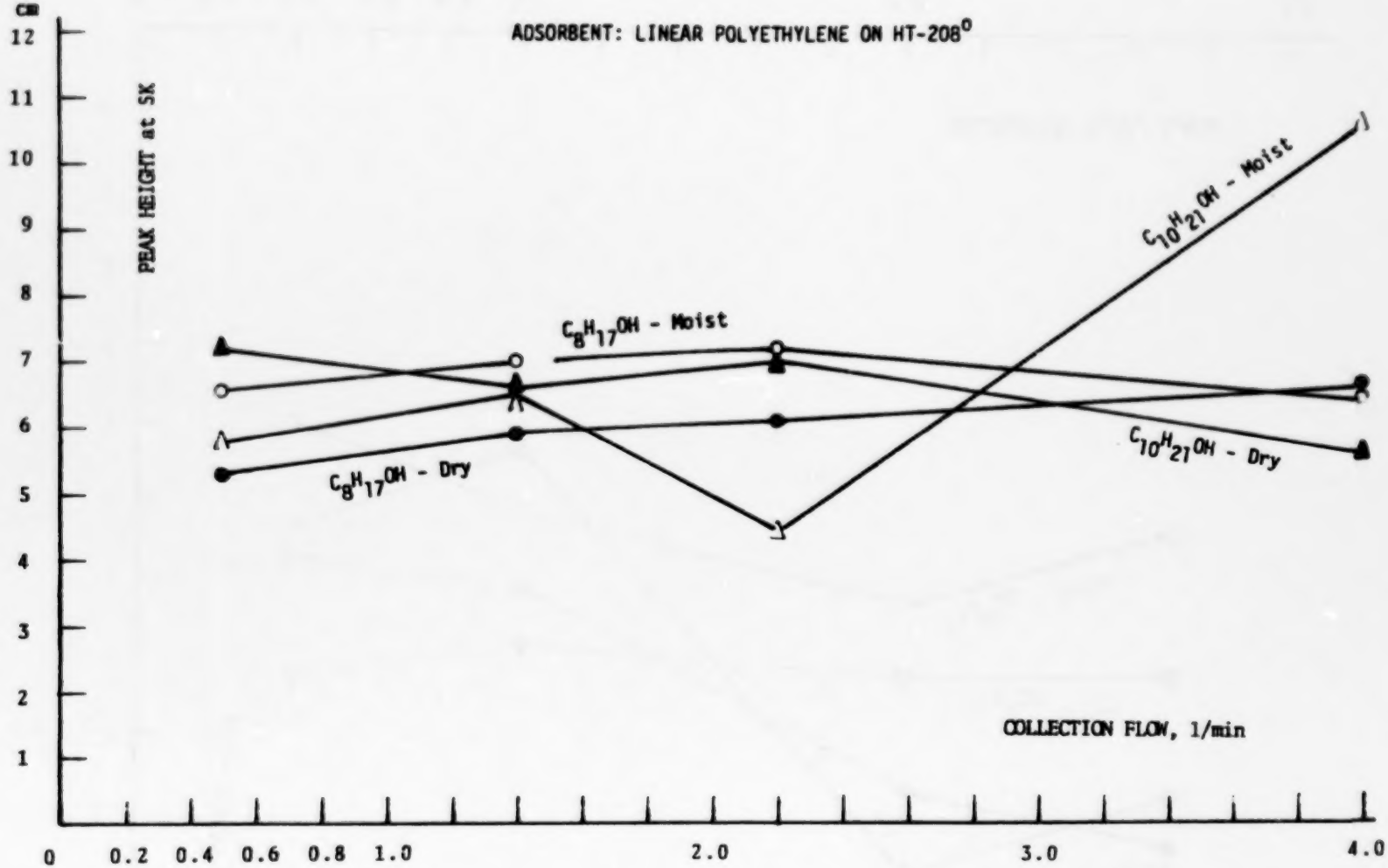
RELATIVE DEGREE OF COLLECTION AS FUNCTIONS OF HUMIDITY AND FLOW RATES

Figure 22



RELATIVE DEGREE OF COLLECTION AS FUNCTIONS OF HUMIDITY AND FLOW RATES

Figure 23



RELATIVE DEGREE OF COLLECTION AS FUNCTIONS OF HUMIDITY AND FLOW RATES

Figure 24

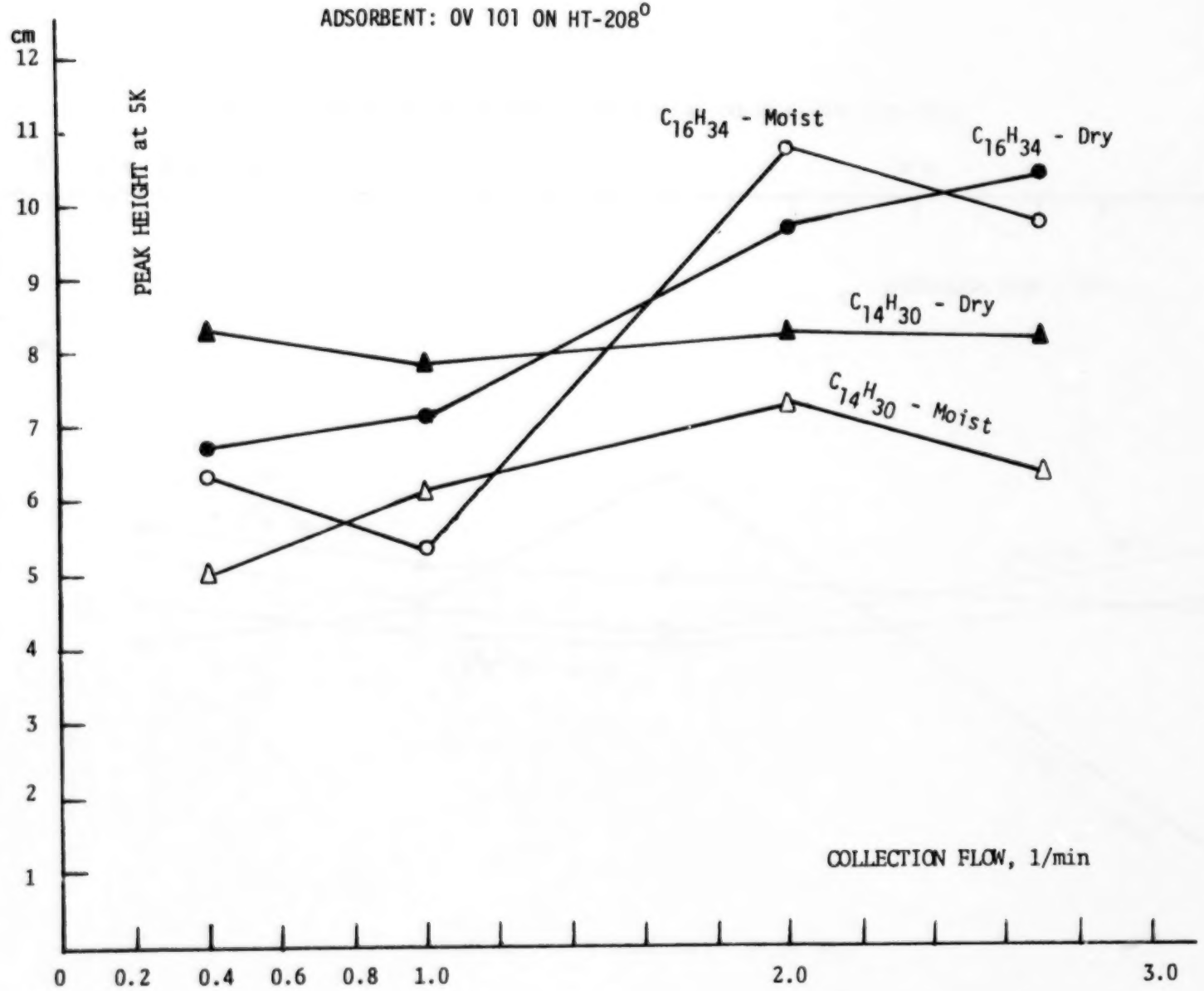
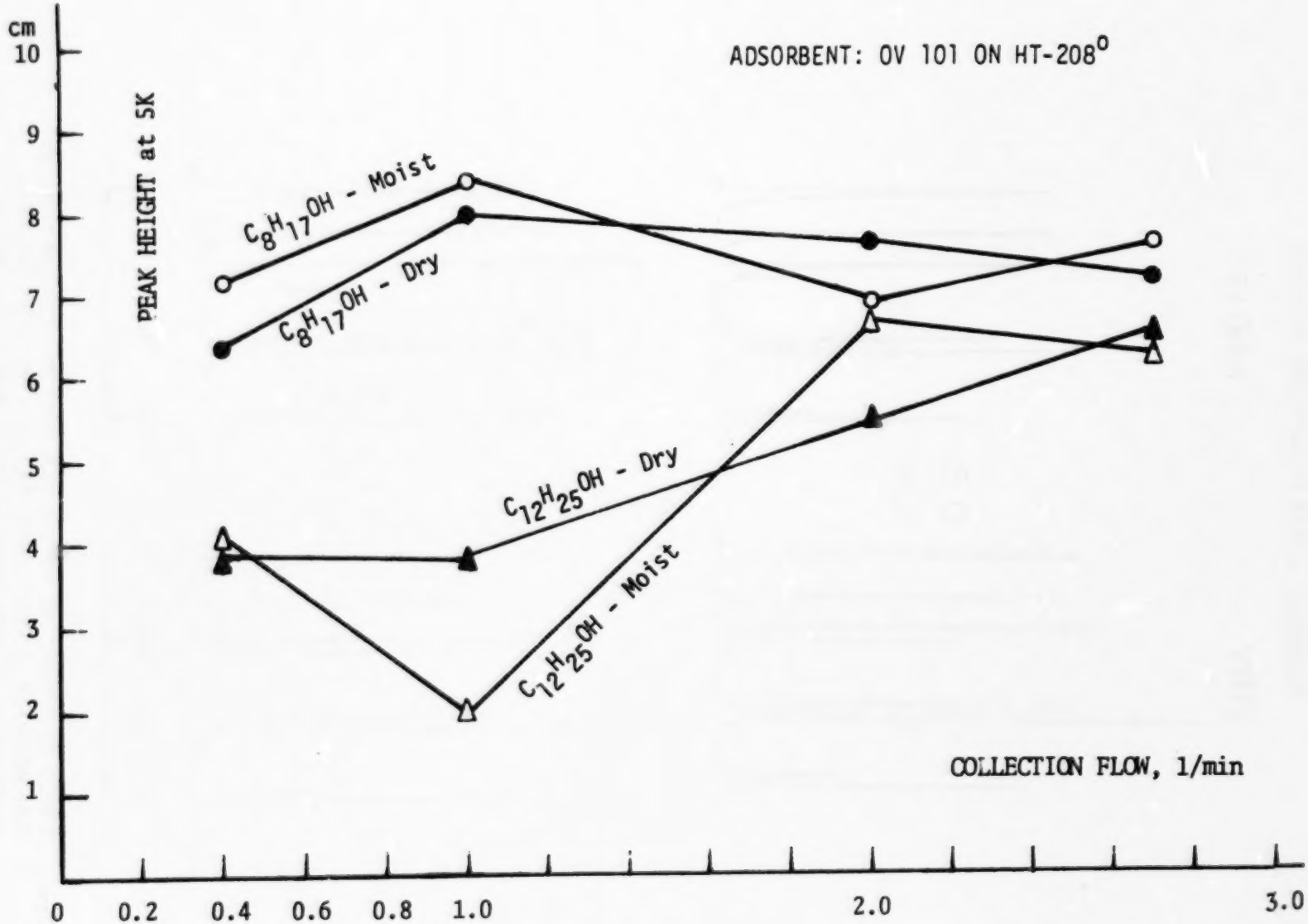


Figure 25 RELATIVE DEGREE OF COLLECTION AS FUNCTIONS OF HUMIDITY AND FLOW RATES



RELATIVE DEGREE OF COLLECTION AS FUNCTIONS OF HUMIDITY AND FLOW RATES

Figure 26

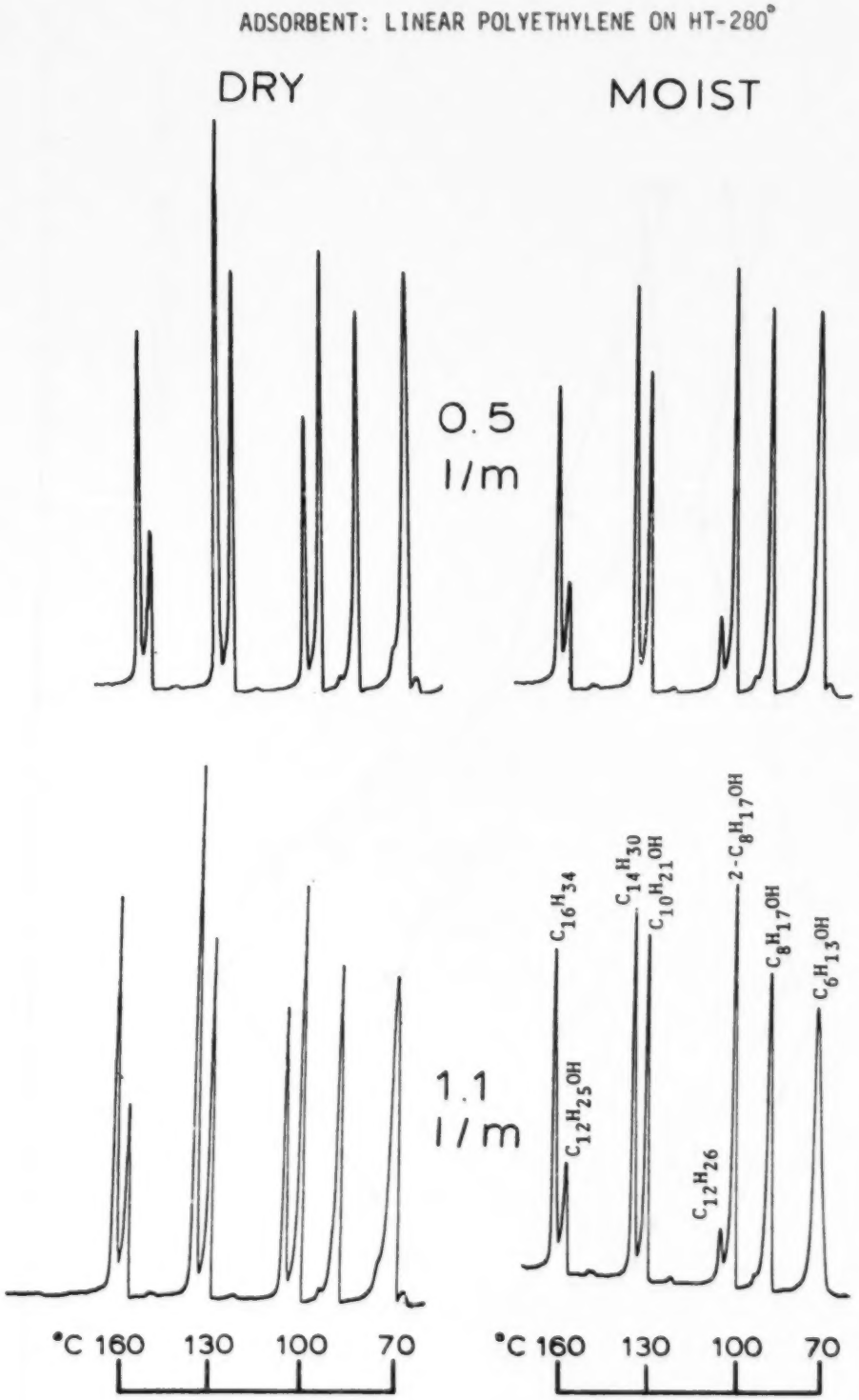


Figure 27(a) EFFECTS OF HUMIDITY AND SAMPLING FLOW RATES ON COLLECTION EFFICIENCY. HEAT DESORPTION INTRODUCTION SYSTEM, 190°; FID, 225°; ANALYTICAL COLUMN: 3% OV 17 ON CHROMOSORB W,100-120 MESH, 6 FT.X 2MM I.D. BOROSILICATE; PROGRAM RATE, 8°/ MIN.

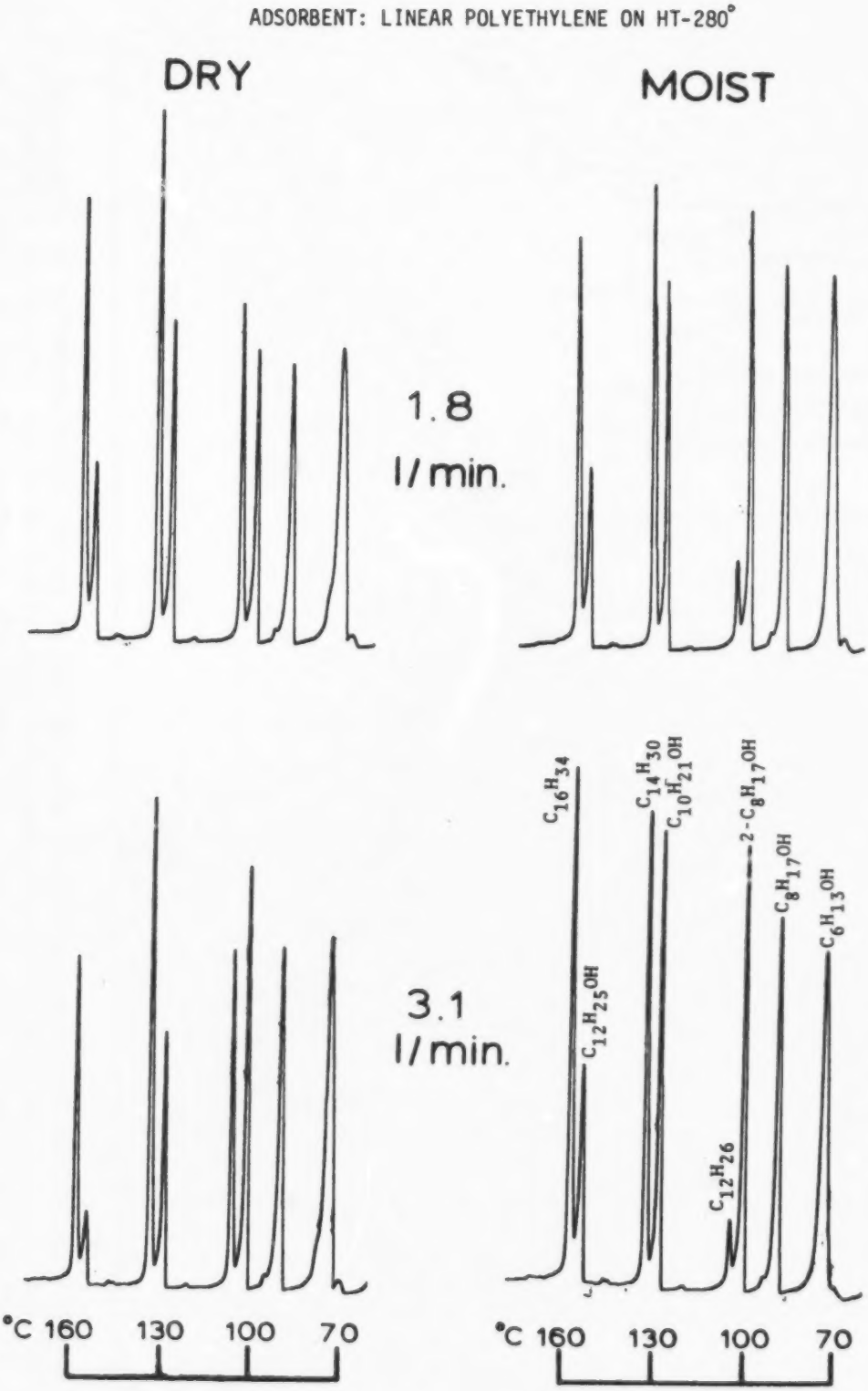
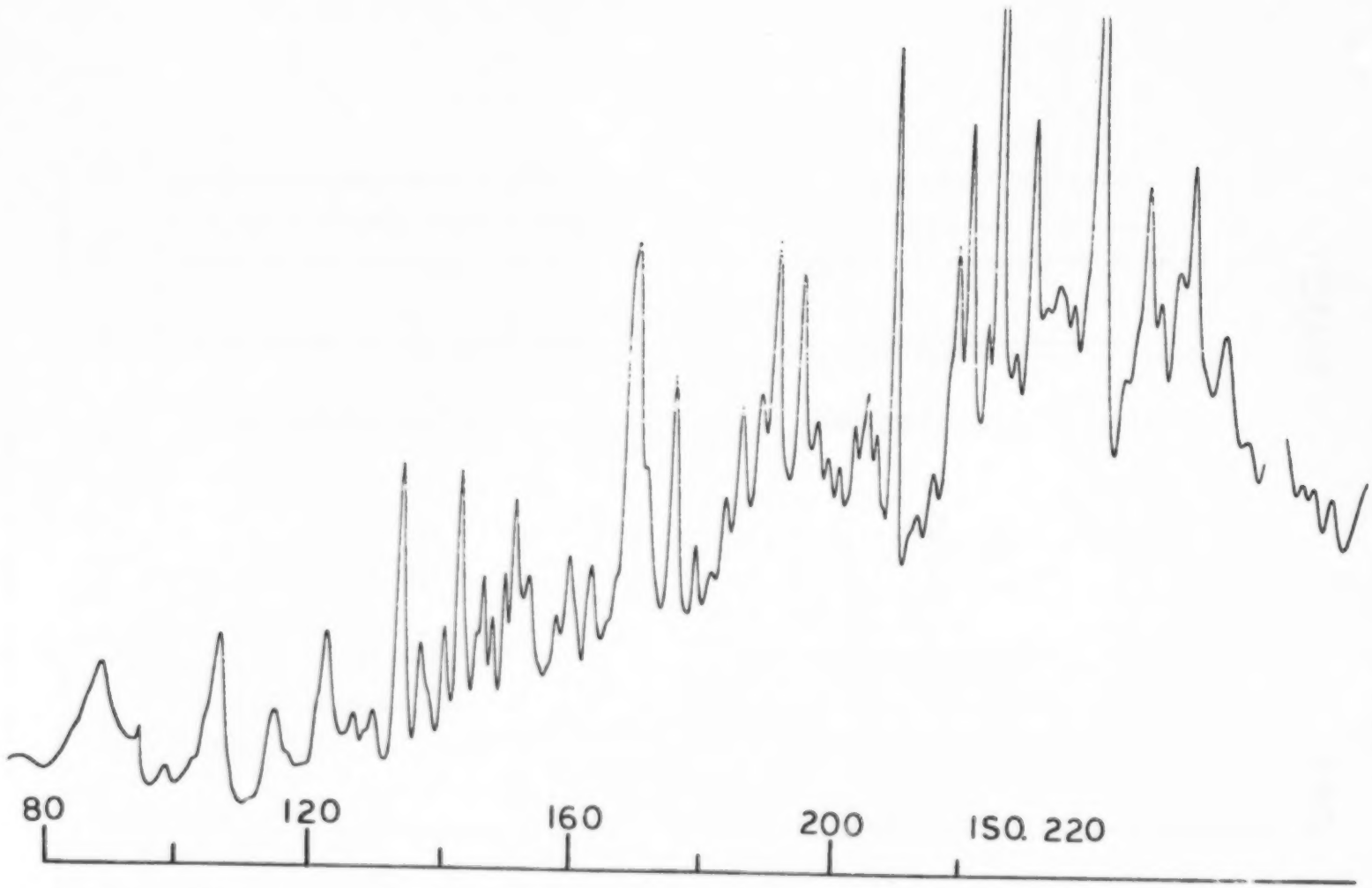
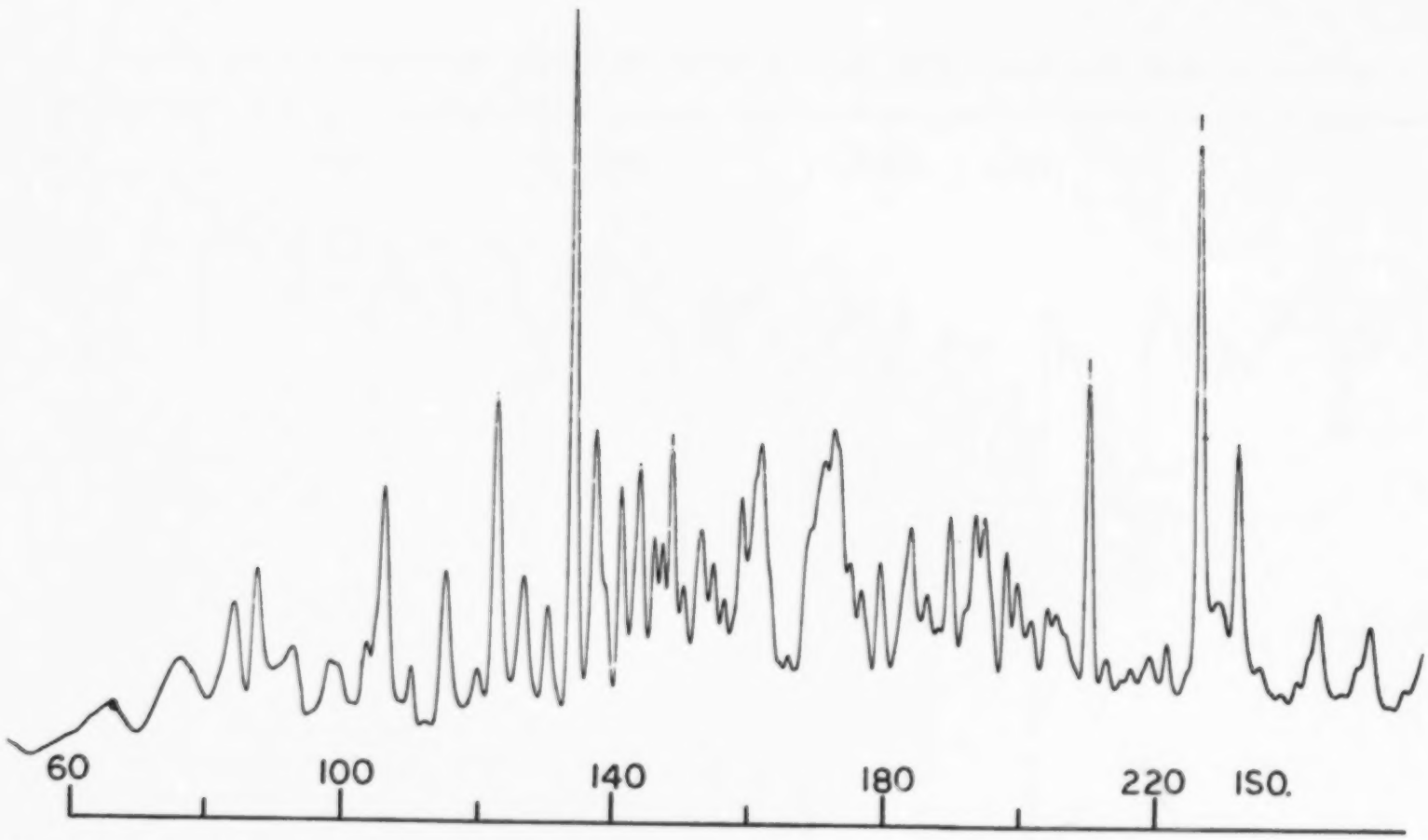


Figure 27(b). same as Figure 27(a)



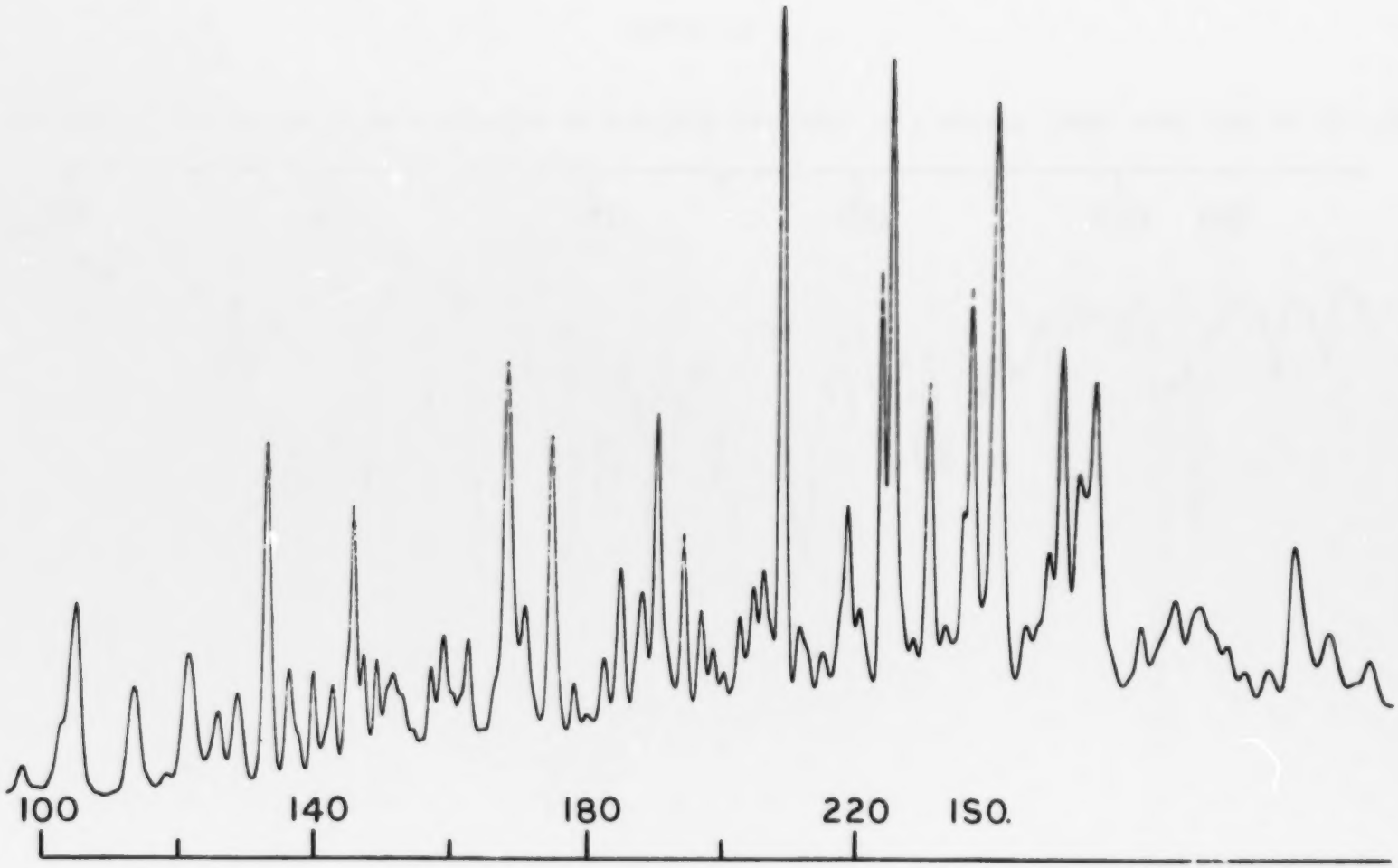
FIVE MINUTES COLLECTION BEHIND A CAR EXHAUST WITH THE ENGINE IDLING; SOLID ADSORBENT IS HYDROTHERMALLY TREATED (208°) SILICA GEL 62 MODIFIED WITH NON-EXTRACTABLE LAYERS OF OV 101; COLLECTION FLOW RATE, 2L/MIN; HEAT DESORPTION TEMPERATURE, 190°; FID TEMP, 225°; ANALYTICAL COLUMN IS 10% FFAP ON CHROMOSORB W, AW, DMCS, 80-100 MESH;X 500; 20 FT X 2 MM I.D. BOROSILICATE LOOP TUBE;

Figure 28



TEN MINUTES COLLECTION IN AN ATMOSPHERE OF GASOLINE CONTAINED IN A BEAKER. CONDITIONS SAME AS FIG. 28.

Figure 29



FIFTEEN MINUTES COLLECTION BEHIND AN IDLING STATION WAGON. CONDITIONS SAME AS FIG. 28.

Figure 30

SECTION 5

RESULTS AND DISCUSSION

Since this work is a multi-faceted endeavor, the results and discussion for each phase of the work are given immediately after each experimental procedure. This provides a systematized organizational concept to enable the reader to consult the chromatograms which are an integral part of the results and discussion section of each phase.

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Based on Work Supported by EPA Grant R-801050

PUBLICATIONS

Research which was totally or partially supported by the EPA grant R-801050.

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